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Amidoximes Provide Facile Platinum(II)-Mediated Oxime−Nitrile Coupling

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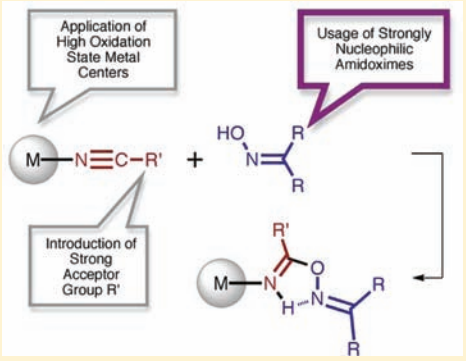
Supporting Information

ABSTRACT: The nucleophilic addition of amidoximes R′C(NH_2)═NOH [R′ = Me (**2.Me**), Ph (**2.Ph**)] to coordinated nitriles in the platinum(II) complexes *trans*-[$PtCl_2$(RCN)$_2$] [R = Et (**1t.Et**), Ph (**1t.Ph**), NMe_2 (**1t.NMe$_2$**)] and *cis*-[$PtCl_2$(RCN)$_2$] [R = Et (**1c.Et**), Ph (**1c.Ph**), NMe_2 (**1c.NMe$_2$**)] proceeds in a 1:1 molar ratio and leads to the monoaddition products *trans*-[PtCl(RCN)-{HN═C(R)ONC(R′)NH_2}]Cl [R = NMe_2; R′ = Me ([**3a**]Cl), Ph ([**3b**]Cl)], *cis*-[$PtCl_2${HN═C(R)ONC(R′)NH_2}] [R = NMe_2; R′ = Me (**4a**), Ph (**4b**)], and *trans*/*cis*-[$PtCl_2$(RCN){HN═C(R)ONC(R′)NH_2}] [R = Et; R′ = Me (**5a**, **6a**), Ph (**5b**, **6b**); R = Ph; R′ = Me (**5c**, **6c**), Ph (**5d**, **6d**), correspondingly]. If the nucleophilic addition proceeds in a 2:1 molar ratio, the reaction gives the bisaddition species *trans*/*cis*-[Pt{HN═C(R)ONC(R′)NH_2}$_2$]Cl_2 [R = NMe_2; R′ = Me ([**7a**]Cl_2, [**8a**]Cl_2), Ph ([**7b**]Cl_2, [**8b**]Cl_2)] and *trans*/*cis*-[$PtCl_2${HN═C(R)ONC(R′)NH_2}$_2$] [R = Et; R′ = Me (**10a**), Ph (**9b**, **10b**); R = Ph; R′ = Me (**9c**, **10c**), Ph (**9d**, **10d**), respectively]. The reaction of 1 equiv of the corresponding amidoxime and each of [**3a**]Cl, [**3b**]Cl, **5b**−**5d**, and **6a**−**6d** leads to [**7a**]Cl_2, [**7b**]Cl_2, **9b**−**9d**, and **10a**−**10d**. Open-chain bisaddition species **9b**−**9d** and **10a**−**10d** were transformed to corresponding chelated bisaddition complexes $[\mathbf{7d}]^{2+}$−$[\mathbf{7f}]^{2+}$ and $[\mathbf{8c}]^{2+}$−$[\mathbf{8f}]^{2+}$ by the addition of 2 equiv $AgNO_3$. All of the complexes synthesized bear nitrogen-bound O-iminoacylated amidoxime groups. The obtained complexes were characterized by elemental analyses, high-resolution ESI-MS, IR, and ^{1}H NMR techniques, while **4a**, **4b**, **5b**, **6d**, [**7b**]$(Cl)_2$, [**7d**]$(SO_3CF_3)_2$, [**8b**]$(Cl)_2$, [**8f**]$(NO_3)_2$, **9b**, and **10b** were also characterized by single-crystal X-ray diffraction.



INTRODUCTION

Nucleophilic addition to nitriles, RC≡N, represents an attractive route to new organic and coordination compounds with a variety of laboratory and industrial applications. The reactivity of nitriles has already been summarized in some comprehensive reviews,[1−10] giving an idea that these compounds, in particular unreactive RCN species bearing donor R groups, should be subjected to additional electrophilic activation in order to perform the nucleophilic addition. One of the most effective routes to reach this activation is coordination to a metal center.

Although nucleophilic addition to metal-activated nitriles has been studied for almost a century, only in the past decade were these reactions extended to HON nucleophiles.[9] In particular, reactions between ligated nitriles at kinetically inert metal centers (e.g., platinum[11−15] or rhodium[16,17]) and HON species such as "simple" oximes,[13−22] *vic*-dioximes,[23] and functionalized oximes[11,24−29] lead to the formation of the C−O{N} bond upon addition of the OH group at the C≡N moiety. Moreover, when these reactions were performed at kinetically labile metal centers (e.g., Co^{II},[30] Ni^{II},[20,21,31−36] and Zn^{II}[37]), they acquired an applied significance insofar as they opened some efficient routes to syntheses of important classes of nitrile-derived organic compounds such as amidines,[30] acylamides,[34] 1,3,5-triazapentadienes,[32−36,38,39] carboxamides[37,40−44] and related species,[45,46] and phthalocyanines.[21,47] The latter findings made a strong impact on the further exploration of the nitrile reactions with HON-type nucleophiles.

The results of the synthetic studies (see above) and also the performed theoretical considerations[22,48,49] on the addition of HON nucleophiles to ligated nitriles allowed verification of the major driving forces of the reaction (Scheme 1). Thus, this transformation could be enhanced by affecting the nitrile from its different sides, viz., the C and/or N atoms. This group of methods includes the application of high oxidation metal centers (e.g., Pt^{IV},[11,12,24,28] Re^{IV},[50] and Rh^{III}[16,17]) and/or the involvement of electron-deficient RCN (e.g., R = CO_2Et, CH_2Cl) ligands.[13,14]

In principle, yet another route to promote the reaction is an increase of the nucleophilicity of oxime species (Scheme 1). However, conventional ketoximes and aldoximes usually exhibit rather similar nucleophilic properties, displaying a leveling effect in the addition. Thus, the latter approach for the enhancement—based on the application of oximes of a

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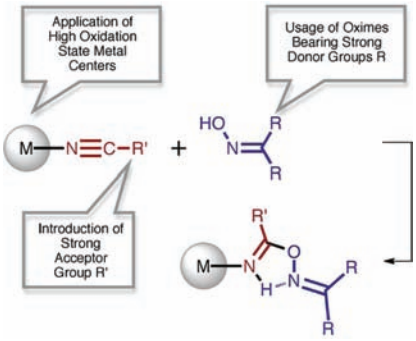
Scheme 1. Enhancement of Nucleophilic Additions of Oximes to Nitriles



higher nucleophilicity—was never synthetically explored in the past.

Recently, we found that *amidoximes* are more reactive nucleophiles than dialkylketoximes toward coupling with RCN ligands at a Pt^{IV} center.[11] Furthermore, our preliminary kinetic data indicate that, in the addition to ligated nitriles, the amidoxime $Ph(NH_2)C{=}NOH$ is approximately an order of magnitude stronger than $Ph(Me)C{=}NOH$.[50] In the current work, we decided to amplify the reaction of amidoximes to rather unreactive $(RCN)Pt^{II}$ species, especially those where R is a donor group. It is worth mentioning that previously only three works dealt with the Pt^{II}-mediated nucleophilic addition of oximes, and they all include the reaction with reactive nitriles such as dialkylcyanamides or electron-deficient conventional nitriles.[13,14,18]

Our particular interest in studying the addition of amidoximes to nitrile ligands in platinum(II) complexes was at least 4-fold. First, we expected to explore a novel approach to the addition of oximes to metal-bound nitriles based on the application of highly reactive oximes. Second, we were interested in the extension of metal-mediated amidoxime–nitrile coupling, previously reported for Pt^{IV} centers,[11,12,23] to Pt^{II} species. Third, we anticipated the study of the relative reactivity of dialkylcyanamides and aryl- and alkylcyanides bound to Pt^{II} centers. Fourth, it was planned to shed light on the differences in the reactivity of the nitrile complexes in different cis/trans configurations.

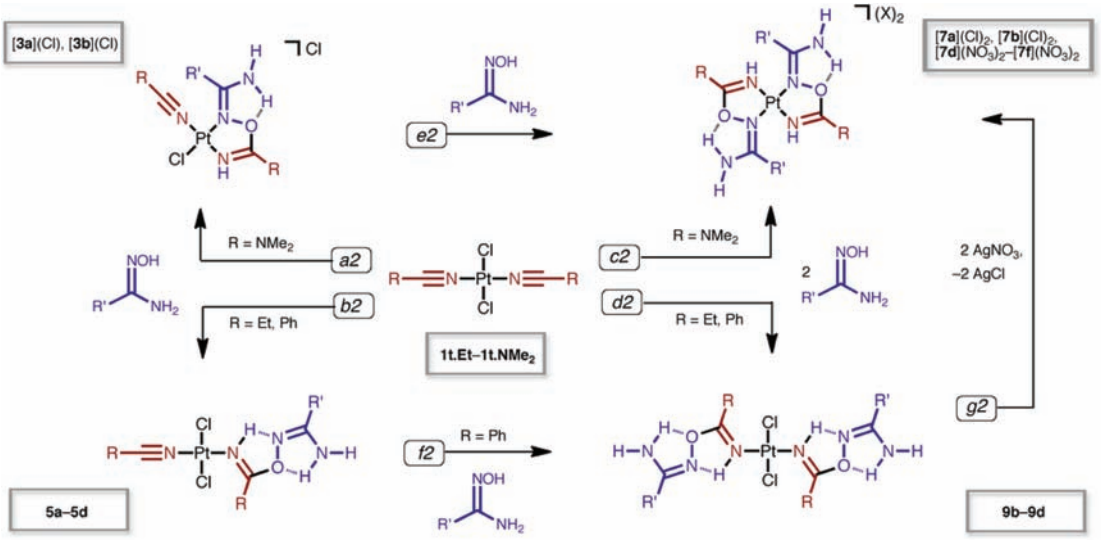
RESULTS

As starting materials, we addressed, on the one hand, the nitrile platinum(II) complexes *trans*-$[PtCl_2(RCN)_2]$ [R = Et (**1t.Et**),[51] Ph (**1t.Ph**),[52] NMe_2 (**1t.NMe$_2$**)[53]] and *cis*-$[PtCl_2(RCN)_2]$ [R = Et (**1c.Et**),[51] Ph (**1c.Ph**),[52] NMe_2 (**1c.NMe$_2$**)[53]] and, on the other hand, the amidoximes $R'C(NH_2){=}NOH$ [R′ = Me (**2.Me**), Ph (**2.Ph**)[54]]. The reaction of **1t.Et**–**1t.NMe$_2$** and **1c.Et**–**1c.NMe$_2$** with **2.Me** or **2.Ph** (in all possible combinations) proceeds at room temperature (RT) at both 1:1 and 1:2 molar ratios of the reactants (except **1t.Et**, where the reaction stops after the addition of 1 equiv of amidoximes; see later) and affords complexes bearing iminoacylated oxime species (Schemes 2 and 3 and Table 1). Synthetic experiments are described in sections that follow.

Reaction between the (Nitrile)platinum(II) Complexes with 1 equiv of Amidoximes. The direction of the reaction between platinum(II) nitrile complexes **1t** and **1c** and amidoximes **2.Me** or **2.Ph** depends on the cis/trans configuration of the starting metal complex and the nature of the R group of the coordinated nitrile. Compounds **1t.Et**, **1t.Ph**, **1c.Et**, and **1c.Ph**, featuring coordinated alkyl- or arylcyanides, react with 1 equiv of **2.Me** or **2.Ph** (in all possible combinations) to form open-chain monoaddition species **5a**–**5d** (Scheme 2, *b2*) and **6a**–**6d** (Scheme 3, *b3*), which were isolated in 55–92% yield. In contrast to these alkyl- or arylcyanide complexes, dimethylcyanamide-based compounds **1t.NMe$_2$** and **1c.NMe$_2$** react with 1 equiv of **2.Me** or **2.Ph** (in all possible combinations) to form cationic [**3a**](Cl) and [**3b**](Cl) (Scheme 2, *a2*) and neutral chelates **4a** and **4b** (Scheme 3, *a3*).

Reaction of the (Nitrile)platinum(II) Complexes with 2 equiv of Amidoximes. Complexes [**3a**](Cl), [**3b**](Cl), **5c**, **5d**, and **6a**–**6d** (see later for reactions of **5a** and **5b**), derived from monoaddition, were converted to corresponding bisaddition species [**7a**](Cl)$_2$, [**7b**](Cl)$_2$, **9c**, and **9d** (Scheme 2, *e2* and *f2*) and **10a**–**10d** (Scheme 3, *e3*) by the reaction with 1 equiv more of the corresponding amidoxime. Alternatively,

Scheme 2. Synthetic Transformations of 1t



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Scheme 3. Synthetic Transformations of 1c

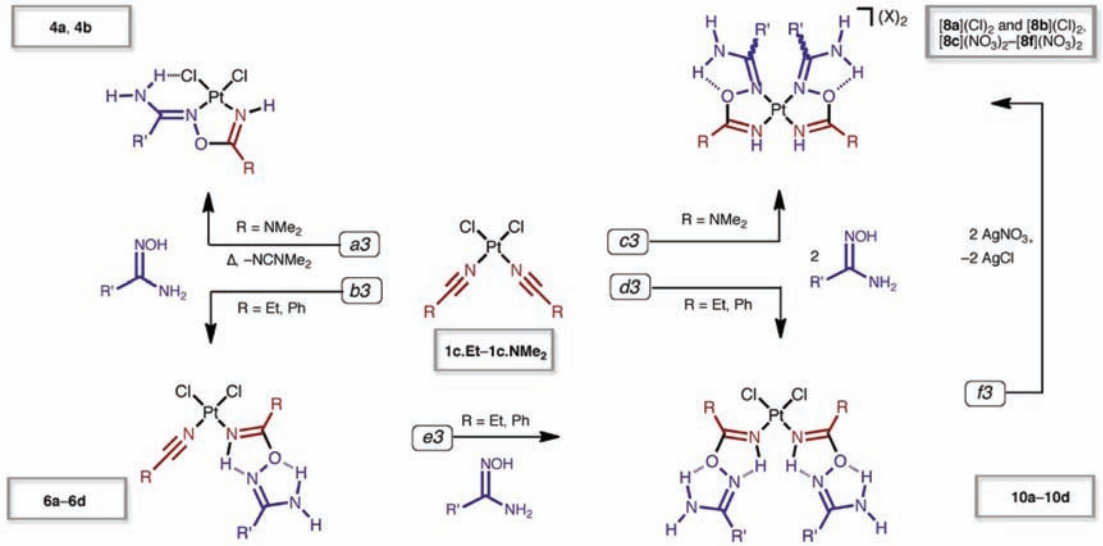

Table 1. Compound Numbering and Preparative Yields of the Obtained Species

no.	R	R′	yield	no.	R	R′	yield	no.	R	R′	yield
[**3a**](Cl)	NMe_2	Me	73	**6c**	Ph	Me	55	[**8d**]$(NO_3)_2$	Et	Ph	~100
[**3b**](Cl)	NMe_2	Ph	82	**6d**	Ph	Ph	70	[**8e**]$(NO_3)_2$	Ph	Me	~100
4a	NMe_2	Me	62	[**7a**]$(Cl)_2$	NMe_2	Me	73	[**8f**]$(NO_3)_2$	Ph	Ph	~100
4b	NMe_2	Ph	75	[**7b**]$(Cl)_2$	NMe_2	Ph	82	**9b**	Et	Ph	33
5a	Et	Me	74	[**7d**]$(NO_3)_2$	Et	Ph	~100	**9c**	Ph	Me	83
5b	Et	Ph	92	[**7e**]$(NO_3)_2$	Ph	Me	~100	**9d**	Ph	Ph	87
5c	Ph	Me	57	[**7f**]$(NO_3)_2$	Ph	Ph	~100	**10a**	Et	Me	66
5d	Ph	Ph	82	[**8a**]$(Cl)_2$	NMe_2	Me	62	**10b**	Et	Ph	69
6a	Et	Me	71	[**8b**]$(Cl)_2$	NMe_2	Ph	75	**10c**	Ph	Me	81
6b	Et	Ph	83	[**8c**]$(NO_3)_2$	Et	Me	~100	**10d**	Ph	Ph	87

[**7a**]$(Cl)_2$, [**7b**]$(Cl)_2$, **9c**, and **9d** (Scheme 2, *c2* and *d2*), and [**8a**]$(Cl)_2$, [**8b**]$(Cl)_2$, and **10a**–**10d** (Scheme 3, *c3* and *d3*) were obtained by the reaction of starting nitrile complexes **1.t** and **1.c** with 2 equiv of **2.Me** or **2.Ph** (in all possible combinations) in a $MeNO_2$ solution for 10–100 h at RT (isolated yields 62–87%). Descriptions of these reactions are given in the next two sections.

a. Reaction of [PtCl$_2$(RCN)$_2$] (R = Et, Ph) with 2 equiv of Amidoximes. The direction of the reaction between the platinum(II) propiononitrile complexes (**1t.Et** and **1c.Et**) and amidoxime **2.Me** or **2.Ph** depends on the cis/trans configuration of the starting metal species. The reaction of *trans*-[$PtCl_2(EtCN)_2$] (**1t.Et**) with 2 equiv of **2.Me** or **2.Ph** in nitromethane at RT completes after 2 days and brings about a broad mixture of unidentified products. However, we were able to synthesize the bisaddition product **9b** via the reaction of *trans*-[$PtCl_2$(EtCN){HN=C(Et)ON=C(NH_2)Ph}] (**5b**) with 1 equiv of **2.Ph** for 2 days in MeOH at RT, which leads to precipitation of the crystalline *trans*-[$PtCl_2${HN=C(Et)-ON=C(NH_2)Ph}$_2$]·2MeOH (**9b**) in 33% isolated yield along with many unidentified products that remain in the solution. An analogous reaction of **5a** with **2.Me** under the same reaction conditions leads to a mixture of platinum-containing species in solution, and no precipitate was formed.

Complex *cis*-[$PtCl_2(EtCN)_2$] (**1c.Et**) reacts with 2 equiv of **2.Me** or **2.Ph** for 2 days in $MeNO_2$ at RT to produce the bisaddition products *cis*-[$PtCl_2${HN=C(Et)ON=C(NH_2)R}$_2$] in good yields (66% for **10a** and 69% for **10b**; Scheme 3). Benzonitrile species **1t.Ph** and **1c.Ph** react with 2 equiv of **2.Me** or **2.Ph** for 1 day in a nitromethane solution at RT to produce the bisaddition products [$PtCl_2${HN=C(Ph)ON=C(NH_2)-R}$_2$] (**9c**, **9d**, **10c**, and **10d**).

b. Reaction of [PtCl$_2$(NCNMe$_2$)$_2$] with 2 equiv of Amidoximes. Compounds **1t.NMe$_2$** and **1c.NMe$_2$** react with 2 equiv of **2.Me** or **2.Ph** to furnish isomeric bischelates [**7a**]$(Cl)_2$, [**7b**]$(Cl)_2$, [**8a**]$(Cl)_2$, and [**8b**]$(Cl)_2$ (Schemes 2 and 3), Complex **1t.NMe$_2$** in the reaction forms bisaddition chelates [**7a**]$(Cl)_2$ and [**7b**]$(Cl)_2$ for 10 h (vs 20 min for the monoaddition products [**3a**](Cl) and [**3b**](Cl)) in nitromethane at RT in 73% and 82% yields for R′ = Me and Ph, correspondingly, while **1c.NMe$_2$** in the reaction with 2 equiv **2.Me** or **2.Ph** (10 h, $MeNO_2$, RT) gives a broad mixture of unidentified species. Bischelates [**8a**]$(Cl)_2$ and [**8b**]$(Cl)_2$ were generated more selectively and isolated in rather good yields (62% and 75% for R′ = Me and Ph, respectively) only at −8 °C (100 h, $MeNO_2$).

Chelation Promoted by Chloride Abstraction. We found that bisaddition species derived from propiononitrile (**10a** and **10b**; Scheme 3) and benzonitrile complexes (**9c** and **9d** in Scheme 2 and **10c** and **10d** in Scheme 3) do not convert to corresponding chelated complexes [**7e**]$(Cl)_2$, [**7f**]$(Cl)_2$, and [**8c**]$(Cl)_2$–[**8f**]$(Cl)_2$ in a $MeNO_2$ solution at 100 °C or in the solid phase at temperatures ca. 5 °C lower than the corresponding decomposition temperatures for these complexes. However, chelates [**7e**]$(NO_3)_2$, [**7f**]$(NO_3)_2$, and [**8c**]$(NO_3)_2$–[**8f**]$(NO_3)_2$ were obtained from **9c** and **9d**

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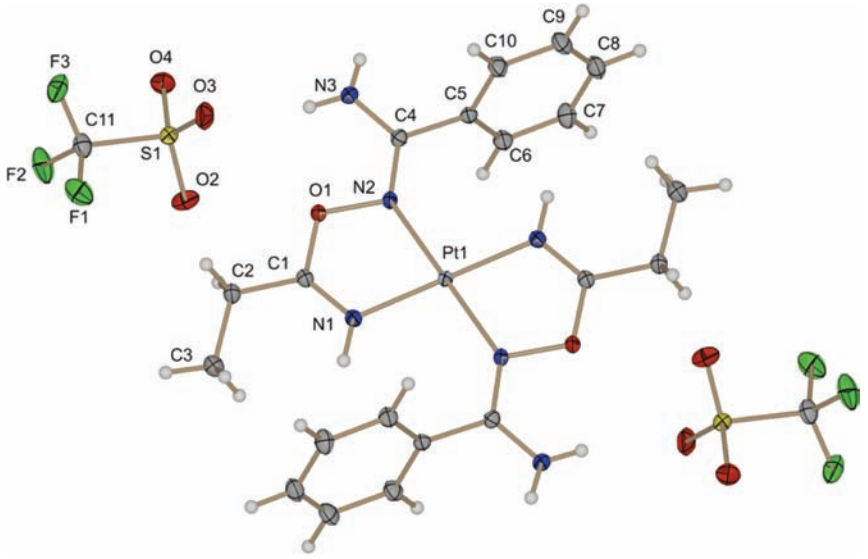

Figure 1. Molecular structure of $[\mathbf{7d}](SO_3CF_3)_2$ with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.2788(17); N2−C4 1.3132(16); N3−C4 1.3249(17).

(Scheme 2, *g2*) and **10a**−**10d** (Scheme 3, *f3*), respectively, by abstraction of the chloride ligands with 2 equiv of $AgNO_3$.

Thus, bischelate $[\mathbf{7d}](NO_3)_2$ was generated by the reaction of **9b** with 2 equiv of $AgNO_3$ for 30 min in MeOH at RT to give $[\mathbf{7d}](NO_3)_2$ in almost quantitative yield. The application of $AgSO_3CF_3$ in this reaction could not be recommended as a synthetic method insofar as all reaction products exhibit similar solubilities and their separation is a rather difficult task. However, by conducting this experiment, we succeeded in isolating a few crystals of $[\mathbf{7d}](SO_3CF_3)_2$ suitable for a single-crystal X-ray diffraction study (see later), confirming the formulation of the cation. The reaction of **1t.Et** and **2.Me** does not give the corresponding bischelate when it was carried out in diverse solvents (MeOH, EtOH, and $MeNO_2$), employing different silver salts ($AgNO_3$ and $AgSO_3CF_3$), and at various temperatures ranging from −8 to +50 °C.

Analytical and Spectroscopy Data. The complexes give satisfactory C, H, and N elemental analyses for the proposed formulas and were also characterized by high-resolution electrospray ionization mass spectrometry (ESI-MS), IR, and ^{1}H NMR spectroscopy. Cationic species $[\mathbf{8c}](NO_3)_2$ and $[\mathbf{8d}](NO_3)_2$, as an exception, are not sufficiently stable, and they start to decompose right after their formation. However, we succeeded in providing their characterization by IR, high-resolution ESI-MS, and ^{1}H NMR spectroscopy.

In the IR spectra of the obtained complexes, the Pt^{II}-bound imines exhibit medium-to-strong bands at 3496−3058 cm^{-1}, which can be attributed to the N−H stretches. The spectra also display one or two C═N absorption bands in the range of 1674−1588 cm^{-1} specific for the iminoacylated oximes.[55] No bands assignable to C≡N stretches from the (nitrile)platinum(II) species were observed in the spectra of both mono- and bisaddition species **4a**, **4b**, **5a**−**5d**, **6a**−**6d**, $[\mathbf{7a}](Cl)_2$, $[\mathbf{7b}](Cl)_2$, $[\mathbf{7d}](NO_3)_2$−$[\mathbf{7f}](NO_3)_2$, $[\mathbf{8a}](Cl)_2$, $[\mathbf{8b}](Cl)_2$, $[\mathbf{8c}](NO_3)_2$−$[\mathbf{8f}](NO_3)_2$, **9b**−**9d**, and **10a**−**10d**, whereas each of monoaddition complexes [**3a**](Cl) and [**3b**](Cl) exhibits medium-to-strong intensity bands due to ν(C≡N) at 2312 and 2295 cm^{-1}, respectively.

Positive-mode high-resolution ESI-MS spectra of nonionic species display peaks corresponding to the quasi-ion $[M + H]^+$ and/or ions $[M + NH_4]^+$, $[M + Na]^+$, and $[M + K]^+$ or fragmentation ions, i.e., $[M - Cl]^+$ and $[M - 2Cl - H]^+$; the latter fragmentations are typical for platinum(II) chloride complexes. The spectra of ionic species display peaks corresponding to the cations $[M - Cl]^+$ ($[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$), $[M - 2Cl]^{2+}$ ($[\mathbf{7a}]^{2+}$, $[\mathbf{7b}]^{2+}$, $[\mathbf{8a}]^{2+}$, and $[\mathbf{8b}]^{2+}$), and $[M - 2NO_3]^{2+}$ ($[\mathbf{7d}]^{2+}$−$[\mathbf{7f}]^{2+}$ and $[\mathbf{8c}]^{2+}$−$[\mathbf{8f}]^{2+}$) or fragmentation ions $[M - H - 2Cl]^+$ ($[\mathbf{7a}]^{2+}$, $[\mathbf{7b}]^{2+}$, $[\mathbf{8a}]^{2+}$, and $[\mathbf{8b}]^{2+}$) and $[M - H - 2NO_3]^+$ ($[\mathbf{7d}]^{2+}$−$[\mathbf{7f}]^{2+}$, and $[\mathbf{8c}]^{2+}$−$[\mathbf{8f}]^{2+}$).

In the ^{1}H NMR spectra of **4a**, **4b**, $[\mathbf{7a}](Cl)_2$, $[\mathbf{7b}](Cl)_2$, $[\mathbf{7d}](NO_3)_2$−$[\mathbf{7f}](NO_3)_2$, $[\mathbf{8a}](Cl)_2$, $[\mathbf{8b}](Cl)_2$, and $[\mathbf{8c}](NO_3)_2$−$[\mathbf{8f}](NO_3)_2$, one set of signals was observed, whereas the spectra of [**3a**](Cl), [**3b**](Cl), **5a**−**5d**, and **6a**−**6d** exhibit two sets of signals in a 1:1 ratio, viz., from the imine and the nitrile. The characteristic feature of the ^{1}H NMR spectra of **5a**−**5d**, **6a**−**6d**, **9b**, **9d**, **10b**, and **10d** is the presence of two broad signals in a low-field region with an integral intensity 1:2 recognized as the N*H* and NH_2 resonances, while the spectra of **9c**, **10a**, and **10c** exhibit three broad signals in a 1:1:1 ratio with different chemical shifts of the amide group protons. The ^{1}H NMR spectra of chelates [**3a**](Cl), [**3b**](Cl), **4a**, **4b**, $[\mathbf{7a}](Cl)_2$, $[\mathbf{7b}](Cl)_2$, $[\mathbf{7d}](NO_3)_2$−$[\mathbf{7f}](NO_3)_2$, $[\mathbf{8a}](Cl)_2$, $[\mathbf{8b}](Cl)_2$, and $[\mathbf{8c}](NO_3)_2$−$[\mathbf{8f}](NO_3)_2$ display three signals of the NH protons, which are situated in a lower field relative to the open-chain species **5a**−**5d**, **6a**−**6d**, **9b**−**9d**, and **10a**−**10d**. In [**3b**](Cl) and **4b**, signals of the dimethylamino group are shifted to a higher field relative to [**3a**](Cl) and **4a** (ca. 0.3−0.4 ppm), and this effect may be caused by the shielding influence of the phenyl group. The same influence of the aromatic ring probably causes a high-field shift of one of the *o*- and *m*-H signals in **6c** and **6d** relative to the corresponding geometrical trans isomers **5c** and **5d** (ca. 0.4 ppm for ortho protons and ca. 0.2 ppm for meta protons).

X-ray Determinations. Molecular structures of **4a** (Figure 2), **4b** (Figure S1 in the Supporting Information), **5b** (Figure 5), **6d** (Figure 6), $[\mathbf{7b}](Cl)_2$ (Figure S2 in the Supporting Information), $[\mathbf{7d}](SO_3CF_3)_2$ (Figure 1), $[\mathbf{8b}](Cl)_2$ (Figures 3 and 4), $[\mathbf{8f}](NO_3)_2$ (Figure S3 in the Supporting Information), **9b** (Figure 7), and **10b** (Figure 8) indicate that all coordination polyhedra exhibit typical square-planar geometry. All bond

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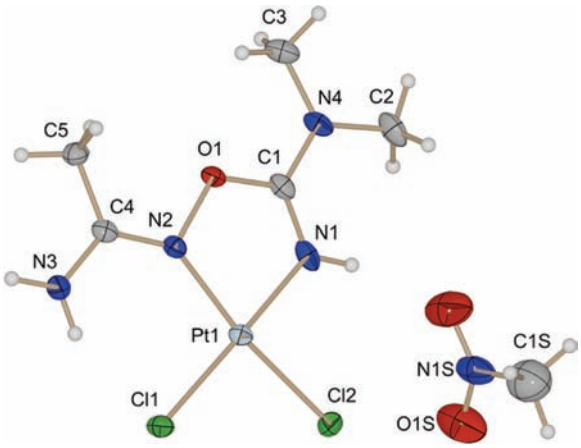

Figure 2. Molecular structure of **4a** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.314(6); N4−C1 1.331(5); N2−C4 1.318(5); N3−C4 1.332(5).

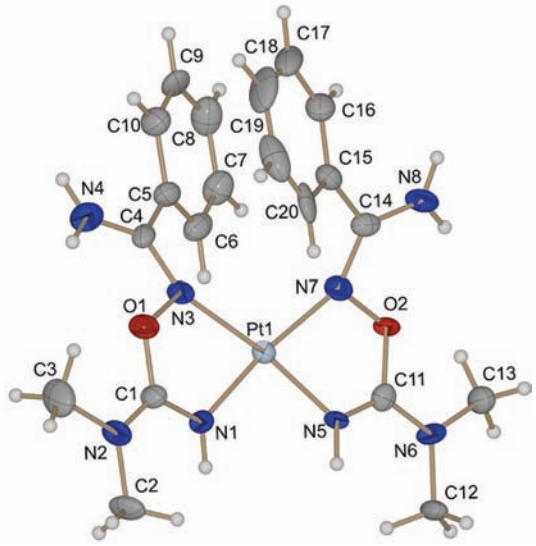

Figure 3. Molecular structure of *P*-[**8b**]$(Cl)_2$ with the atomic numbering scheme. Cl anions are omitted for clarity. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.316(10); N5−C11 1.299(10); N2−C1 1.314(11); N6−C11 1.339(10); N3−C4 1.320(10); N7−C14 1.316(11); N4−C4 1.321(11); N8−C14 1.308(11).

angles around the Pt^{II} centers are close to 90°, except the N−Pt−N angles in the chelates (see below). The Pt−Cl distances [2.2862(12)−2.3193(7) Å] are specific for the Pt^{II}−Cl bonds,[56] the Pt−N_{imine} bond lengths [1.972(2)−2.033(3) Å] exhibit values characteristic for (imine)platinum(II) species,[57] and the Pt−N_{oxime} bond lengths [1.9895(18)−2.020(7) Å] have values characteristic for (oxime)platinum(II) species.[18] Bond lengths and angles of the iminoacylated oxime ligands agree well with those found for other similar (imine)platinum(II) complexes.[13,14,18]

Molecular Structures of Chelates ***4a***, ***4b***, *[**7b**](Cl)$_2$, [**7d**]$(SO_3CF_3)_2$, [**8b**](Cl)$_2$, *and* [**8f**]$(NO_3)_2$ *(Figures 1−4 and S1−S3 in the Supporting Information).* The N−Pt−N angles in the compounds range from 77.07(7) to 79.63(9)°. In [**7d**]$(SO_3CF_3)_2$ and [**8f**]$(NO_3)_2$ (Figures 1 and S3 in the Supporting Information, respectively), the C−N_{imine} bond lengths are typical C=N double bonds, ranging from 1.276(3) to 1.2788(17) Å, while in dimethylcyanamide derivatives **4a**, **4b**, [**7b**]$(Cl)_2$, and [**8b**]$(Cl)_2$ (Figures 2, S1 and S2 in the Supporting Information, 3, and 4, correspondingly), the $(C-N)_{imine}$ bond lengths [1.298(3)−1.316(10) Å] and C−NMe_2 distances [1.314(11)−1.339(10) Å] have intermediate order because conjugation between them. Another conjugation is observed between the C−N_{oxime} and C−NH_2 bonds [bond lengths equal to 1.3132(16)−1.330(3) and 1.314(3)−1.333(4) Å, respectively]. The C−O [1.3349(15)−1.363(10) Å] and O−N [1.4446(14)−1.472(8) Å] bond lengths are the normal single bonds.[57]

In [**7b**]$(Cl)_2$, [**7d**]$(SO_3CF_3)_2$, and [**8b**]$(Cl)_2$ (Figures S2 in the Supporting Information, 1, 3, and 4, respectively), the oxime C=N bonds in both ligands exhibit the *E* configuration, while in **4a** and **4b** (Figures 2 and S1 in the Supporting Information), the C=N bonds are in the *Z* form, and [**8f**]$(NO_3)_2$ (Figure S3 in the Supporting Information) features two ligands in the different *E*/*Z* configurations. In the *E*-configured ligands, the intramolecular hydrogen bonding is formed between the NH_2 group and the oxime O atom [N···O 2.463−2.583 Å; N−H···O 95.97−105.21°]. In **4a** and **4b** (Figures 2 and S1 in the Supporting Information) bearing the *Z*-iminoacylated ligands, the hydrogen bond is formed between the NH_2 center and the Cl atom [N···Cl 3.099(4) and 3.092(3) Å; N−H···Cl 156.8° and 163.1°, respectively]. No intramolecular hydrogen bond was detected in the *Z*-configured ligand of [**8f**]$(NO_3)_2$ (Figure S3 in the Supporting Information).

cis-Bischelates [**8a**]$(Cl)_2$, [**8b**]$(Cl)_2$, and [**8c**]$(NO_3)_2$−[**8f**]-$(NO_3)_2$ exhibit a nonplanar arrangement. The twisted structure provides the existence of the molecules in the isomeric *P* and *M* forms (Figure 4). Two forms for [**8a**]$(Cl)_2$, [**8b**]$(Cl)_2$, and [**8c**]$(NO_3)_2$−[**8f**]$(NO_3)_2$ were observed by single-crystal X-ray diffraction, which was applied to racemic crystals obtained for [**8b**]$(Cl)_2$ (Figures 3 and 4) and [**8f**]$(NO_3)_2$ (Figure S3 in the Supporting Information); both *P* and *M* isomers were observed in the crystal lattices.

Molecular Structures of Open-Chain Species ***5b***, ***6d***, ***9b***, *and* ***10b*** *(Figures 5−8).* All of the C−N_{imine} and C−N_{oxime} bond lengths are typical C=N double bonds,[12,57−59] ranging from 1.251(3) to 1.289(6) Å and from 1.280(6) to 1.305(3) Å, respectively, while the values of the C−NH_2 [1.330(7)−1.345(7) Å], C−O [1.342(3)−1.353(6) Å], and O−N [1.450(2)−1.477(5) Å] bond lengths indicate their single-bond characters.[57] In **5b** and **6d** (Figures 5 and 6, correspondingly), the C−$N_{nitrile}$ bond lengths are typical C≡N triple bonds, ranging from 1.135(6) to 1.147(6) Å.[52,60]

The iminoacylated oxime ligands are in the *E* form, which is stabilized via the intramolecular hydrogen bonding between the imino H atom and the uncomplexed oxime N atom [N···N 2.578(6)−2.623(6) Å; N−H···N 112.56−122.0°]; the same type of hydrogen bonding was previously observed for other open-chain N-bound iminoacylated oximes.[12,23,28,58,59] Another intramolecular hydrogen bridge is formed between NH_2 and the oxime O atom [N···O 2.506−2.561 Å; N−H···O 94.07−104.93°].

DISCUSSION

a. Differences in the Reactivity between Amidoximes and Ketoximes. Earlier work[18] explicitly shows that the activation of aryl- and alkylcyanides by platinum(II) is insufficient for the nucleophilic addition of the ketoximes R'_2C=NOH

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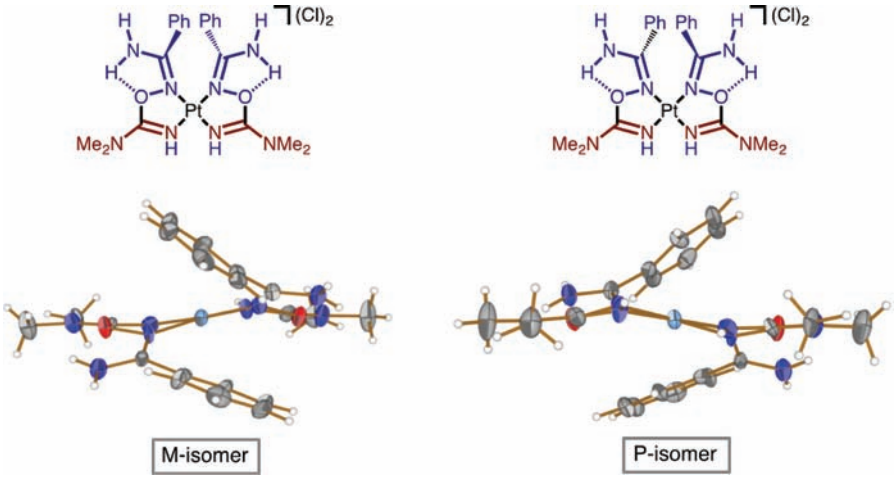

Figure 4. Isomerism for $[\mathbf{8b}](Cl)_2$.

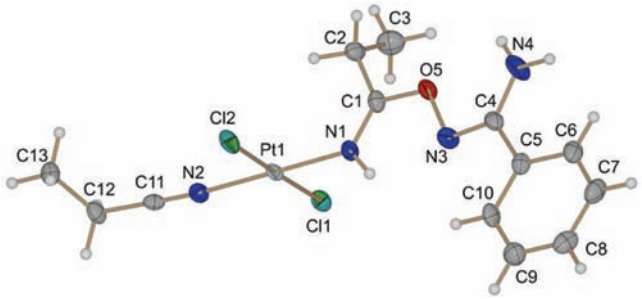

Figure 5. Molecular structure of **5b** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.289(6); N2−C11 1.147(6); N3−C4 1.280(6); N4−C4 1.345(7).

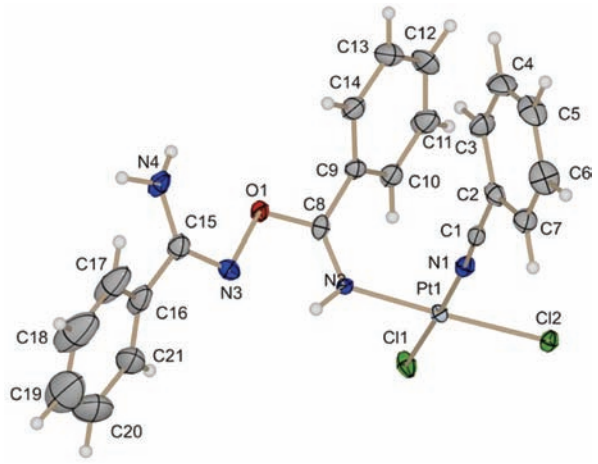

Figure 6. Molecular structure of **6d** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N2−C8 1.277(6); N1−C1 1.136(6); N3−C15 1.291(6); N4−C15 1.330(7).

(R'_2 = Me_2; C_4H_8) to RCN ligands. Only in the case of *cis*-$[Pt(NCNR_2)_2(PPh_3)_2]^{2+}$ (R = Me, Et) were the chelated monoaddition products obtained when Ag^+ or Cu^{2+} was used as an additional activator, which, as believed, metalates the NR_2 group (Scheme 4).[18]

Later, the platinum(II)-mediated reaction of oximes with RCN ligands was extended to electron-deficient nitriles, i.e., with R = Ph, CH_2Cl, and CH_2CO_2Me. The reaction proceeds at 40−50 °C and/or under microwave treatment to produce monodentately coordinated *O*-imidoyloximes in moderate yields (Scheme 5).[13,14]

Herein we demonstrated that the nucleophilic addition of amidoxime **2.Me** or **2.Ph** to $(RCN)_2Pt^{II}$ species **1t** and **1c** proceeds at RT and even at −8 °C [for $[\mathbf{8a}](Cl)_2$ and $[\mathbf{8b}](Cl)_2$] to accomplish the iminoacylated species in good yields. These observations supported our experimental observations[11] (see the Introduction section) that amidoximes are much more reactive nucleophiles than dialkylketoximes because of the +M effect of the NH_2 group.

b. Differences in the Reactivity between Coordinated Dialkylcyanamide and Aryl- and Alkylcyanides. Dimethylcyanamide complexes **1t.NMe$_2$** and **1c.NMe$_2$** react with amidoximes to produce chelates [**3a**](Cl), [**3b**](Cl), **4a**, **4b**, $[\mathbf{7a}](Cl)_2$, $[\mathbf{7b}](Cl)_2$, $[\mathbf{8a}](Cl)_2$, and $[\mathbf{8b}](Cl)_2$, while alkyl- and arylcyanide complexes **1t.Et**, **1t.Ph**, **1c.Et**, and **1c.Ph** react with **2.Me** and **2.Ph** to form open-chain species **5a−5d**, **6a−6d**, **9b−9d**, and **10a−10d**. This observation could be accounted for by the reduced energy barrier of the imine C═N bond isomerization because of conjugation with the NMe_2 group. In our previous work,[11] a similar *Z* configuration was observed for relevant platinum(IV) complexes despite the open-chain nature of the coordinated imines.

Although the reactions of **1t** and **1c** with 1 and 2 equiv of **2.Me** or **2.Ph** proceed at substantially different times (20 min to 48 h), they give structurally similar products. We observed that **1t.NMe$_2$** and **1c.NMe$_2$** react with **2.Me** or **2.Ph** faster than **1t.Ph** and **1c.Ph**, which, in turn, under similar reaction conditions react faster than **1t.Et** and **1c.Et**. The obtained data indicate that the reactivity of platinum(II)-bound nitriles toward the nucleophilic addition of amidoximes **2.Me** and **2.Ph** decreases in the following order, viz., dimethylcyanamide > benzonitrile > propiononitrile ligands. The same reactivity trend was previously observed by our group, and this phenomenon can be explained by the crossover in frontier molecular orbitals control of the nucleophilic addition, specific for dialkylcyanamides.[61]

c. Differences in the Reactivity between the *cis*- and *trans*-(Nitrile)$_2$platinum(II) Complexes. Most reactive dimethylcyanamide complexes **1t.NMe$_2$** and **1c.NMe$_2$** react with 1 equiv of **2.Me** or **2.Ph**, and the reaction proceeds in different directions. In the case of **1t.NMe$_2$**, the reaction occurs as a nucleophilic addition of amidoxime (**2.Me** or **2.Ph**), followed

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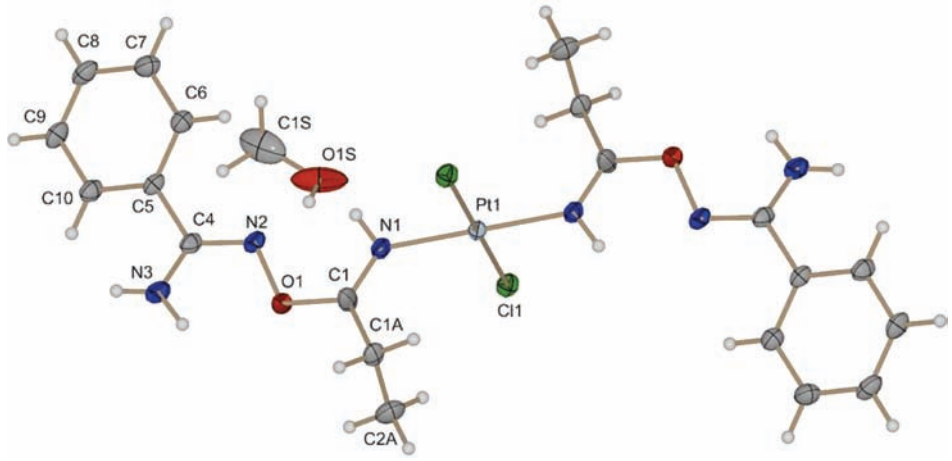


Figure 7. Molecular structure of **9b** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.251(3); N2−C4 1.305(3); N3−C4 1.334(3).

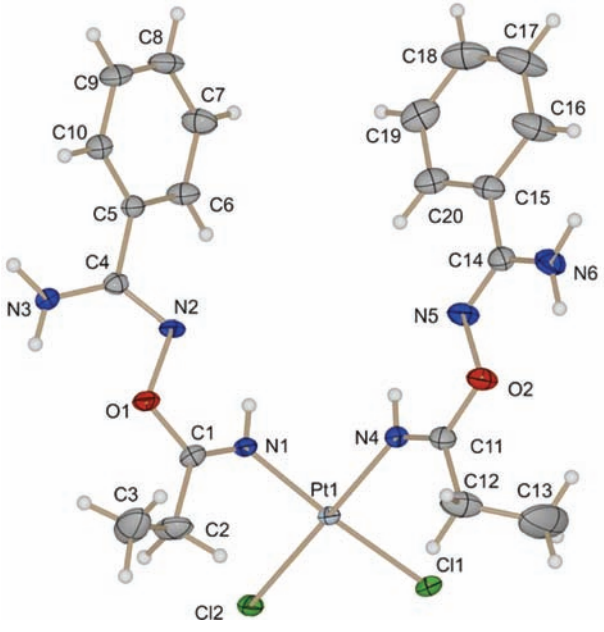
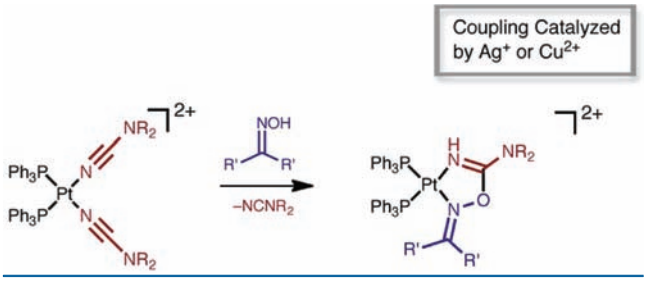


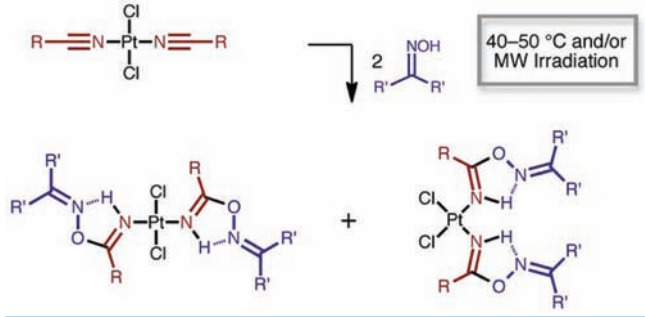
Figure 8. Molecular structure of **10b** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Selected bond lengths (Å): N1−C1 1.254(5); N4−C11 1.263(4); N2−C4 1.301(4); N3−C4 1.334(4); N5−C14 1.299(5); N6−C14 1.339(5).

Scheme 4. Lewis Acid Catalyzed Ketoxime−(Nitrile)platinum(II) Coupling



by intramolecular substitution of a chloride ligand, while **1c.NMe$_2$** reacts with 1 equiv of **2.Me** and **2.Ph** to produce **4a** and **4b** derived from the nucleophilic addition, followed by the substitution of dimethylcyanamide. Apparently, the elimination of neutral dimethylcyanamide from the neutral complex is more feasible than the elimination of chloride from the positively charged complex. Compound **1t.NMe$_2$** reacts with 2 equiv of **2.Me** or **2.Ph** at RT in good yields, while the reaction of **1c.NMe$_2$** under the same conditions leads to a broad spectrum of unidentified products.

Scheme 5. Microwave-Irradiation-Induced Ketoxime−(Nitrile)platinum(II) Coupling



In summary, the results from this work could be considered from at least three perspectives. First, we observed that amidoximes are more reactive than ketoximes and aldoximes, and this observation is coherent with the general idea that the NH_2 moiety increases the nucleophilicity of the oxime group because of the +M effect. Hence, the amidoxime species could serve as candidates for the metal-mediated oxime−nitrile coupling when a metal center does not provide sufficient activation for the performance of this reaction. Furthermore, other types of functionalized oximes, e.g., alkylhydroximic acids and their thio analogues and also hydroxyguanidines, should also have an enhanced nucleophilicity. The coupling of these species with nitrile ligands is currently under investigation in our group. Second, the reactivity of platinum(II)-bound RCN species decreases in the order dimethylcyanamide > benzonitrile > propiononitrile. Third, the reactivity of *cis*-(nitrile)$_2$platinum(II) complexes toward the addition of amidoximes is higher than that of trans complexes; these trends point out to the more reactive substrates for the coupling.

EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. The amidoximes were synthesized by literature methods.[54] Complexes [$PtCl_2$(RCN)$_2$]

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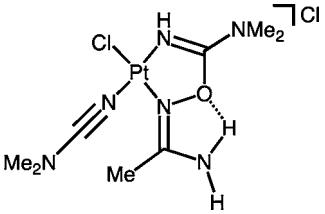
(R = Et,[52] Ph,[51] NMe_2[53]) were synthesized in accordance with the published procedures; the cis and trans isomers were separated by column chromatography on SiO_2 (Silicagel 60 F_{254}, 0.063−0.200 mm, Merck). C, H, and N elemental analyses were carried out by the Department of Organic Chemistry of St. Petersburg State University on a Hewlett-Packard 185B carbon−hydrogen−nitrogen analyzer. ESI-MS spectra were obtained on a Bruker micrOTOF spectrometer equipped with an ESI source. The instrument was operated in both positive- and negative-ion mode using a range of m/z 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS) and the capillary exit at ±(70−150) V. The nebulizer gas flow was 0.4 bar and the drying gas flow 4.0 L/min. For ESI, species were dissolved in MeOH or MeCN. In the isotopic pattern, the most intensive peak is reported. Thin-layer chromatography (TLC) was performed on Silufol UV254 SiO_2 plates. IR spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. ^1H NMR spectra were measured on a Bruker DPX 300 spectrometer at ambient temperature in Me_2SO-d_6 and $CDCl_3$; residual solvent signals were used as internal standards.

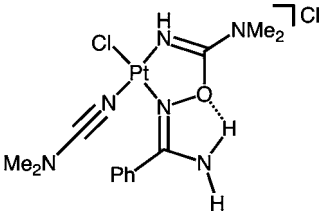
X-ray Structure Determinations. The crystals of all complexes were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Bruker Kappa Apex II, a Bruker Smart Apex II, or a Bruker Kappa Apex II diffractometer using Mo Kα radiation (λ = 0.71073 Å). The *APEX2*[62] software packages were used for cell refinement and data reduction. A semiempirical absorption correction based on equivalent reflections of a numerical absorption correction (*SADABS*[63]) was applied to all data. The structures were solved by direct methods using the *SHELXS-97*,[64] *SIR97*,[65] or *SIR2008*[66] programs with the *WinGX*[67] graphical user interface. Structural refinements were carried out using *SHELXL-97*.[64] The NH H atoms were either located from the difference Fourier map and constrained to ride on their parent atom with U_{iso} = 1.5U_{eq} (parent atom) or positioned geometrically with N−H = 0.88 and U_{iso} = 1.2U_{eq} (parent atom). In all structures, the NH_2 and OH H atoms were located from the difference Fourier map and constrained to ride on their parent atom with U_{iso} = 1.5U_{eq} (parent atom). In structure **7b**, the H_2O H atoms were located from the difference Fourier map, and in **8b**, they were located by using Nardelli's *HYDROGEN* program.[68] In both cases, the H atoms were constrained to ride on their parent atom with U_{iso} = 1.5U_{eq} (parent atom). All other H atoms were positioned geometrically and constrained to ride on their parent atom with C−H = 0.95−0.99 Å and U_{iso} = 1.2 − 1.5U_{eq} (parent atom).

In **4a**, the CH_3NO_2 solvent molecule was disordered over two sites with equal occupancies. The N1S−C1S bond was constrained to the observed value, and all heavy atoms in CH_3NO_2 were restrained so that their U_{ij} components approximate to isotropic behavior. In **6d**, one of the phenyl rings (C16B−C21B) was disordered over two sites with an occupancy ratio of 0.53/0.47. These rings were constrained to fit in a regular hexagon with C−C = 1.39 Å. Furthermore, the C atoms were constrained to have similar displacement parameters. Another phenyl ring (C16−C21) was also slightly disordered, and therefore the C atoms were restrained so that their U_{ij} components approximate to isotropic behavior. In **8b**, the asymmetric unit contains two platinum complexes, four Cl^- anions, one H_2O solvent molecule, and seven CH_3NO_2 solvent molecules. Five of the CH_3NO_2 molecules were included in the final structure model. A series of geometric and displacement restraints were applied to these solvent molecules. The other two CH_3NO_2 molecules were heavily disordered, and a satisfactory disorder model was found for them. Their contribution to the calculated structure factors was taken into account by using the *SQUEEZE* routine of *PLATON*.[69] However, the missing CH_3NO_2 molecules were taken into account in the unit cell content. The crystal of **9d** was diffracting only weakly. Therefore, satisfactory data completeness could not been obtained. This structure is included only as Supporting Information. In **9b**, the ethyl group (C1−C2) was disordered over two sites with occupancies of 0.55 and 0.45. The crystallographic details of all structures except **9d** are summarized in Tables S1 and S2 in the Supporting Information. The crystallographic parameters of **9d** are given in Table S3 in the Supporting Information.

Synthetic Work. *Nucleophilic Addition of the Amidoximes to the (Nitrile)platinum(II) Complexes. i. Nucleophilic Addition of 1 equiv of R′C(NH$_2$)═NOH (R′ = Me, Ph) to trans-[PtCl$_2$(NCNMe$_2$)$_2$].* A solution of the amidoxime R′C(NH_2)═NOH (R′ = Me, Ph) (0.10 mmol) in nitromethane (3 mL; R′ = Me) or in chloroform (1 mL; R′ = Ph) was added dropwise for 5 min to a stirred solution of *trans*-[$PtCl_2(NCNMe_2)_2$] (0.10 mmol) in nitromethane (1 mL; R′ = Me) or in chloroform (1.5 mL; R′ = Ph). After 20 min, the volume was reduced in vacuo to 0.5 mL, and the oily precipitate that formed (R′ = Ph) crystallized under ultrasound treatment. The crystalline precipitates were separated by filtration, washed by two 1-mL portions of diethyl ether, and dried at RT in air.

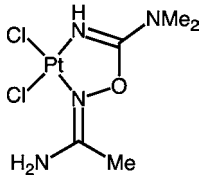


[**3a**](Cl). Yield: 93%. Mp: 152 °C (dec). Anal. Calcd for $C_8H_{18}N_6Cl_2OPt{\cdot}H_2O$: C, 19.28; H, 4.05; N, 16.87. Found: C, 19.39; H, 4.10; N, 16.73. High-resolution ESI^+-MS (MeOH, m/z): 445.095 ($[M - Cl]^+$, calcd 445.082). IR (KBr, selected bonds, cm^{-1}): 3339(m-s), 3204(m), 3159(m-s) [ν(N−H)]; 2312(s) [ν(C≡N)]; 1674(vs), 1655(s) [ν(C═N)]; 1609(m) [δ(N−H) and/or ν(C═N)]; 658(w-m) [δ(C−H)]. ^1H NMR (DMSO-d_6, δ): 8.64 (s, br, 1H, N*H*), 7.86 (s, br, 1H, NH_2), 7.57 (s, br, 1H, NH_2), 3.07 (s, 6H, NMe_2), 2.97 (s, 6H, NMe_2), 2.12 (s, 3H, CH_3).



[**3b**](Cl). Yield: 67%. Mp: 104 °C (dec). Anal. Calcd for $C_{13}H_{20}N_6Cl_2OPt{\cdot}2H_2O$: C, 27.00; H, 4.18; N, 14.53. Found: C, 26.85; H, 4.21; N, 14.34. High-resolution ESI^+-MS (MeOH, m/z): 436.052 ($[M - Cl - NCNMe_2]^+$, calcd 436.045), 507.107 ($[M - Cl]^+$, calcd 507.098), 1012.203 ($[2M - H - 2Cl]^+$, calcd 1012.189). IR (KBr, selected bonds, cm^{-1}): 3416(s), 3358(s), 3290(m) [ν(N−H)]; 3045(vw), 2995(vw), 2932(w) [ν(C−H)]; 2295(m-s) [ν(C≡N)]; 1666(s), 1626(vs) [ν(C═N)]; 1603(m), 1576(m) [δ(N−H) and/or ν(C═N)]; 781(m), 706(m) [δ(C−H)]. ^1H NMR (DMSO-d_6, δ): 8.88 (s, br, 1H, NH_2), 8.56 (s, br, 1H, NH_2), 7.75−7.70 (m, 4H, N*H* + *o*- and *p*-C*H*), 7.61 (t, 2H, *m*-C*H*), 3.13 (s, 6H, NMe_2), 2.58 (s, 6H, NMe_2).

ii. Nucleophilic Addition of 1 equiv of R′C(NH$_2$)═NOH (R′ = Me, Ph) to cis-[PtCl$_2$(NCNMe$_2$)$_2$]. A solution of *cis*-[$PtCl_2(NCNMe_2)_2$] (0.10 mmol) in nitromethane (1 mL) was added to a solution of the amidoxime R′C(NH_2)═NOH (0.15 mmol; R′ = Me, Ph) in nitromethane (10 mL at 60 °C for R′ = Me; 2 mL at RT for R′ = Ph). The solution was kept for 6 h (R′ = Me) or for 18 h (R′ = Ph) at the corresponding temperature, whereupon the solvent was evaporated in vacuo at RT. The residue formed was washed with one 1-mL portion of cold (−5 °C) chloroform and two 1-mL portions of MeOH:Et_2O (50:50, v/v) and dried at RT in air.



4a. Yield: 63%. Mp: 162 °C (dec). Anal. Calcd for $C_5H_{12}N_4Cl_2OPt$: C, 14.64; H, 2.95; N, 13.66. Found: C, 14.88; H, 3.17; N, 13.48.

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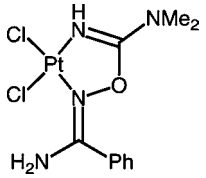
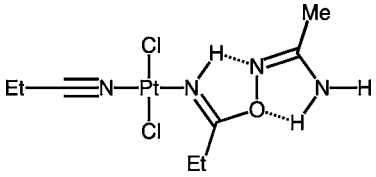
High-resolution ESI$^+$-MS (MeOH:Me_2SO = 10:1, m/z): 432.988 ([M + Na]$^+$, calcd 432.988), 453.046 ([M − Cl + Me_2SO]$^+$, calcd 453.043), 842.989 ([2M + Na]$^+$, calcd 842.987). IR (KBr, selected bonds, cm^{-1}): 3373(vs), 3281(m), 3227(m), 3182(m) [ν(N−H)]; 2966(w), 2935(w), 2887(vw), 2818(vw) [ν(C−H)]; 1661(vs), 1636(s) [ν(C═N)]; 1589(w) [δ(N−H), ν(C═N), and/or ν(C═C)]; 571(m), 530(m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 2:1, v/v): R_f = 0.32. ^{1}H NMR (DMSO-d_6, δ): 7.95 (s, br, 1H, NH_2), 7.89 (s, br, 1H, NH_2), 7.42 (s, br, 1H, NH), 3.00 (s, 6H, NMe_2), 2.16 (s, 3H, CH_3). Crystals suitable for X-ray study were obtained by the slow evaporation of a nitromethane solution at RT in air.

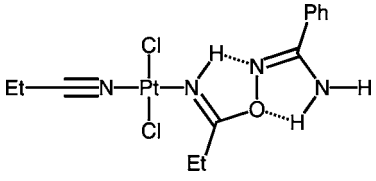


4b. Yield: 94%. Mp: 158 °C (dec). Anal. Calcd for $C_{10}H_{14}N_4Cl_2OPt$: C, 25.43; H, 2.99; N, 11.86. Found: C, 25.17; H, 2.82; N, 11.74. High-resolution ESI$^+$-MS (MeOH, m/z): 490.035 ([M + NH_4]$^+$, calcd 490.048), 494.992 ([M + Na]$^+$, calcd 495.004), 510.963 ([M + K]$^+$, calcd 510.978), 962.030 ([2M + NH_4]$^+$, calcd 962.063), 967.026 ([2M + Na]$^+$, calcd 967.018), 982.996 ([2M + K]$^+$, calcd 982.992), 1439.048 ([3M + Na]$^+$, calcd 1439.032), 1455.011 ([3M + K]$^+$, calcd 1455.006), 1911.069 ([4M + Na]$^+$, calcd 1911.047), 1927.036 ([4M + K]$^+$, calcd 1927.021). IR (KBr, selected bonds, cm^{-1}): 3442(s), 3432(s) [ν(N−H)]; 2961(w), 2923(w), 2853(w) [ν(C−H)]; 1653(m), 1636(m) [ν(C═N)]; 1559(w) [δ(N−H). ν(C═N), and/or ν(C═C)]; 782(w), 705(w), 668(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 5:1, v/v): R_f = 0.31. ^{1}H NMR (DMSO-d_6, δ): 8.36 (s, br, 1H, NH_2), 8.30 (s, br, 1H, NH_2), 7.62−7.50 (m, 5H, Ph), 7.46 (s, br, 1H, NH), 2.71 (s, 6H, NMe_2). Crystals suitable for X-ray study were obtained from the reaction mixture at RT.

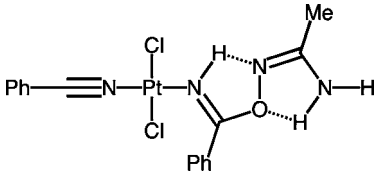
iii. Nucleophilic Addition of 1 equiv of R′C(NH$_2$)═NOH (R′ = Me, Ph) to [PtCl$_2$(RCN)$_2$] (R = Et; Ph). A mixture of the amidoxime R′C(NH_2)═NOH (0.1 mmol; R′ = Me, Ph) and *cis*- or *trans*-[$PtCl_2(RCN)_2$] (0.1 mmol; R = Et; Ph) was dissolved in nitromethane (3 mL). The solution was kept for 3 h at RT, whereupon the solvent was evaporated in vacuo. The residue formed was washed with two 1-mL portions of cold (−5 °C) chloroform and dried at RT in air.



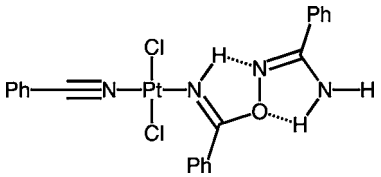
5a. Yield: 74%. Mp: 114 °C (dec). Anal. Calcd for $C_8H_{16}N_4Cl_2OPt\cdot{}^1/_4CHCl_3$: C, 20.64; H, 3.41; N, 11.67. Found: C, 20.81; H, 3.58; N, 11.50. High-resolution ESI$^+$-MS (MeOH, m/z): 378.087 ([M − H − 2Cl]$^+$, calcd 378.084), 415.068 ([M − Cl]$^+$, calcd 415.061), 468.069 ([M + NH_4]$^+$, calcd 468.064), 865.082 ([2M − Cl]$^+$, calcd 865.091), 918.093 ([2M + NH_4]$^+$, calcd 918.094). IR (KBr, selected bonds, cm^{-1}): 3414(m), 3350(s), 3323(s), 3228(m), 3188(m) [ν(N−H)]; 2982(w-m), 2948(w-m), 2921(w), 2884(w) [ν(C−H)]; 1670(m), 1637(vs) [ν(C═N)]; 1607(s), 1569(w) [δ(N−H) and/or ν(C═N)]; 588(w), 536(w-m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 5:1, v/v): R_f = 0.49. ^{1}H NMR ($CDCl_3$, δ): 7.84 (s, br, 1H, NH), 4.86 (s, br, 2H, NH_2), 3.07 (q, 2H, CH_2), 2.80 (q, 2H, CH_2), 1.95 (s, 3H, CH_3), 1.40 (t, 3H, CH_3), 1.38 (t, 3H, CH_3).



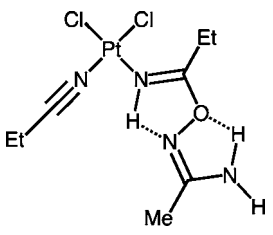
5b. Yield: 92%. Mp: 122 °C (dec). Anal. Calcd for $C_{13}H_{18}N_4Cl_2OPt\cdot H_2O$: C, 29.44; H, 3.80; N, 10.56. Found: C, 29.58; H, 3.51; N, 10.37. High-resolution ESI$^+$-MS (MeOH, m/z): 477.081 ([M − Cl]$^+$, calcd 477.076), 535.039 ([M + Na]$^+$, calcd 535.035), 551.012 ([M + K]$^+$, calcd 551.009), 989.129 ([2M − Cl]$^+$, calcd 989.122), 1047.092 ([2M + Na]$^+$, calcd 1047.081), 1063.062 ([2M + K], calcd 1063.055). IR (KBr, selected bonds, cm^{-1}): 3427(m), 3321(m), 3246(w), 3212(w) [ν(N−H)]; 2986(w), 2944(w), 2917(w), 2881(w) [ν(C−H)]; 1666(w), 1626(s) [ν(C═N) and/or ν(C═C_{Ar})]; 1566(w)]δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 780(w), 696(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 10:1, v/v): R_f = 0.55. ^{1}H NMR ($CDCl_3$, δ): 7.98 (s, br, 1H, NH), 7.64 (d, 2H, *o*-CH), 7.55 (t, 1H, *p*-CH), 7.47 (t, 2H, *m*-CH, Ph), 5.21 (s, br, 2H, NH_2), 3.15 (q, 2H, CH_2), 2.80 (q, 2H, CH_2), 1.47 (t, 3H, CH_3), 1.38 (t, 3H, CH_3). Crystals suitable for X-ray study were obtained by the slow evaporation of an ethanol solution at RT in air.



5c. Yield: 57%. Mp: 136 °C (dec). Anal. Calcd for $C_{16}H_{16}N_4Cl_2OPt\cdot 0.1CHCl_3$: C, 34.64; H, 2.91; N, 10.04. Found: C, 34.74; H, 2.87; N, 9.90. High-resolution ESI$^+$-MS (MeOH, m/z): 474.092 ([M − 2Cl − H]$^+$, calcd 474.084), 511.068 ([M − Cl]$^+$, calcd 511.061). IR (KBr, selected bonds, cm^{-1}): 3454(s), 3413(s), 3264(m) [ν(N−H)]; 3072(w), 2926(m), 2851(w) [ν(C−H)]; 1619(s) [ν(C═N) and/or ν(C═C_{Ar})]; 1576(m) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 781(w), 758(m), 684(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 10:1, v/v): R_f = 0.41. ^{1}H NMR ($CDCl_3$, δ): 8.60 (d, 2H, Ph), 8.32 (s, br, 1H, NH), 7.83−7.50 (m, 8H, Ph), 4.98 (s, br, 2H, NH_2), 2.03 (s, 3H, CH_3).



5d. Yield: 82%. Mp: 136 °C (dec). Anal. Calcd for $C_{21}H_{18}N_4Cl_2OPt\cdot CHCl_3$: C, 36.31; H, 2.63; N, 7.70. Found: C, 36.25; H, 2.53; N, 7.71. High-resolution ESI$^+$-MS (MeOH, m/z): 607.032 ([M − H]$^+$, calcd 607.037), 1181.105 ([2M − Cl]$^+$, calcd 1181.122), 1215.071 ([2M − H]$^+$, calcd 1215.083), 1239.077 ([2M + Na]$^+$, calcd 1239.081). IR (KBr, selected bonds, cm^{-1}): 3489(s), 3439(s), 3268(m) [ν(N−H)]; 3068(w), 2924(m), 2853(w) [ν(C−H)]; 1654(s), 1624(s) [ν(C═N) and/or ν(C═C_{Ar})]; 1567(m) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 755(w), 696(w), 683(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 10:1, v/v): R_f = 0.63. ^{1}H NMR ($CDCl_3$, δ): 8.65 (d, 2H, Ph), 8.45 (s, br, 1H, NH), 7.77−7.48 (m, 13H, Ph), 5.29 (s, br, 2H, NH_2).



6a. Yield: 71%. Mp: 97 °C (dec). Anal. Calcd for $C_8H_{16}N_4Cl_2OPt$: C, 21.34; H, 3.58; N, 12.44. Found: C, 21.47; H, 3.52; N, 12.40. High-resolution ESI$^+$-MS (MeOH, m/z): 378.089 ([M − H − 2Cl]$^+$, calcd

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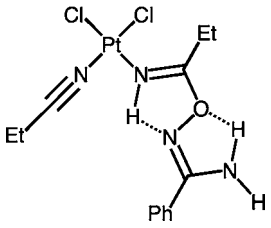
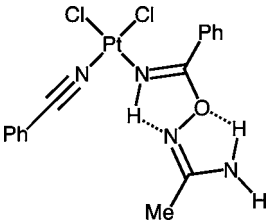
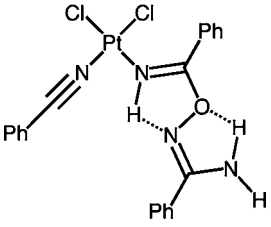
378.084), 415.066 ([M − Cl]$^+$, calcd 415.061), 451.043 ([M + H]$^+$, calcd 451.037), 468.071 ([M + NH_4]$^+$, calcd 468.064), 865.090 ([2M − Cl]$^+$, calcd 865.091), 918.089 ([2M + NH_4]$^+$, calcd 918.094), 939.019 ([2M + K]$^+$, calcd 939.023), 1278.129 ([3M − H − 2Cl]$^+$, calcd 1278.144), 1351.093 ([3M + H]$^+$, calcd 1351.097). IR (KBr, selected bonds, cm^{-1}): 3417(m), 3322(s), 3242(m) [ν(N−H)]; 2988(w), 2948(w-m), 2921(w-m), 2886(w) [ν(C−H)]; 1672(m), 1631(vs) [ν(C═N)]; 1608(s) [δ(N−H) and/or ν(C═N)]; 608(w), 523(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 3:1, v/v): R_f = 0.43. ^{1}H NMR ($CDCl_3$, δ): 7.74 (s, br, 1H, N*H*), 5.06 (s, br, 2H, NH_2), 3.07 (q, 2H, CH_2), 2.80 (q, 2H, CH_2), 2.01 (s, 3H, CH_3), 1.43 (t, 3H, CH_3), 1.38 (t, 3H, CH_3).



6b. Yield: 83%. Mp: 110 °C (dec). Anal. Calcd for $C_{13}H_{18}N_4Cl_2OPt·H_2O$: C, 29.44; H, 3.80; N, 10.56. Found: C, 29.37; H, 3.62; N, 10.66. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 513.064 ([M + H]$^+$, calcd 513.053), 530.091 ([M + NH_4]$^+$, calcd 530.080), 535.047 ([M + Na]$^+$, calcd 535.035), 551.019 ([M + K]$^+$, calcd 551.009), 1042.133 ([2M + NH_4]$^+$, calcd 1042.125), 1047.098 ([2M + Na]$^+$, calcd 1047.081), 1063.063 ([2M + K]$^+$, calcd 1063.055). IR (KBr, selected bonds, cm^{-1}): 3424(s), 3332(m), 3241(m) [ν(N−H)]; 3064(w), 2992(w), 2942(w) [ν(C−H)]; 1599(m) [ν(C═N) and/or ν(C═C_{Ar})]; 1560(m) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 776(w), 752(w), 697(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 2:1, v/v): R_f = 0.61. ^{1}H NMR ($CDCl_3$, δ): 7.89 (s, br, 1H, N*H*), 7.68 (d, 2H, *o*-C*H*), 7.59 (t, 1H, *p*-C*H*), 7.51 (t, 2H, *m*-C*H*, Ph), 5.25 (s, br, 2H, NH_2), 3.15 (q, 2H, CH_2), 2.75 (q, 2H, CH_2), 1.47 (t, 3H, CH_3), 1.38 (t, 3H, CH_3).

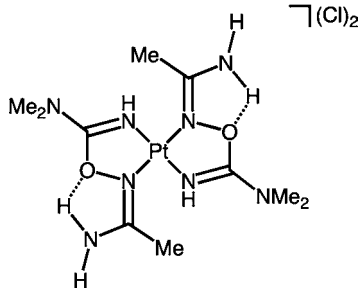


6c. Yield: 55%. Mp: 85 °C (dec). Anal. Calcd for $C_{16}H_{16}N_4Cl_2OPt$: C, 35.18; H, 2.95; N, 10.26. Found: C, 35.24; H, 2.92; N, 10.13. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 546.049 ([M + H]$^+$, calcd 546.043), 563.078 ([M + NH_4]$^+$, calcd 563.069). IR (KBr, selected bonds, cm^{-1}): 3447(s), 3351(s), 3276(m) [ν(N−H)]; 3193(m), 3064(w), 2963(w-m), 2924(w), 2866(w) [ν(C−H)]; 1648(m), 1623(vs) [ν(C═N)]; 1599(m-s) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 805(m), 757(m), 697(m), 684(m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 5:1, v/v): R_f = 0.39. ^{1}H NMR ($CDCl_3$, δ): 8.63 (d, 2H, *o*-C*H*), 8.41 (s, br, 1H, N*H*), 7.64−7.49 (m, 4H, Ph), 7.42 (t, 2H, *m*-C*H*), 7.23 (d, 2H, *o*-C*H*), 5.10 (s, br, 2H, NH_2), 2.06 (s, 3H, CH_3).

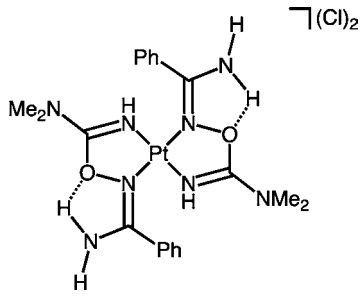


6d. Yield: 70%. Mp: 128 °C (dec). Anal. Calcd for $C_{21}H_{18}N_4Cl_2OPt$: C, 41.46; H, 2.98; N, 9.21. Found: C, 41.24; H, 2.92; N, 9.39. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 609.108 ([M + H]$^+$, calcd 609.053), 626.136 ([M + NH_4]$^+$, calcd 626.080), 631.092 ([M + Na]$^+$, calcd 631.035), 647.066 ([M + K]$^+$, calcd 647.009), 1234.209 ([2M + NH_4]$^+$, calcd 1234.125), 1239.174 ([2M + Na]$^+$, calcd 1239.081), 1255.141 ([2M + K]$^+$, calcd 1255.055). IR (KBr, selected bonds, cm^{-1}): 3417(s), 3326(m), 3206(m) [ν(N−H)]; 3064(w), 2961(m), 2934(w) [ν(C−H)]; 1625(s), 1599(m) [ν(C═N) and/or ν(C═C_{Ar})]; 1565(m) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 775(w), 750(w), 691(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 10:1, v/v): R_f = 0.37. ^{1}H NMR ($CDCl_3$, δ): 8.70 (d, 2H, *o*-C*H*), 8.59 (s, br, 1H, N*H*), 7.72 (d, 2H, *o*-C*H*), 7.66−7.49 (m, 7H, Ph), 7.42 (t, 2H, *m*-C*H*), 7.24 (d, 2H, *o*-C*H*), 5.33 (s, br, 2H, NH_2). Crystals suitable for X-ray study were obtained by the slow evaporation of a nitromethane solution at RT in air.

iv. Nucleophilic Addition of 2 equiv of R′C(NH$_2$)═NOH (R′ = Me, Ph) to cis- and trans-[PtCl$_2$(NCNMe$_2$)$_2$]. A solution of R′C(NOH)-NH_2 (0.2 mmol) in nitromethane (1 mL) (or methanol for R′ = Me) was added to a solution of [$PtCl_2(NCNMe_2)_2$] (0.1 mmol) in nitromethane (2 mL). The homogeneous solution was kept for 10 h at RT (for *trans*-[$PtCl_2(NCNMe_2)_2$]) or 100 h at −8 °C (for *cis*-[$PtCl_2(NCNMe_2)_2$]). The precipitate formed was filtered off, washed with two 2-mL portions of nitromethane, and dried at RT in air.



[**7a**](Cl)$_2$. Yield: 73%. Mp: 225 °C (dec). Anal. Calcd for $C_{10}H_{24}N_8Cl_2O_2Pt·{}^1/_2H_2O$: C, 21.32; H, 4.47; N, 19.89. Found: C, 21.46; H, 4.55; N, 19.75. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 482.155 ([M − 2Cl − H]$^+$, calcd 482.154). IR (KBr, selected bonds, cm^{-1}): 3432(m), 3425(m), 3290(m), 3181(m), 3058(m) [ν(N−H)]; 2925(w), 2853(w), 2824(w) [ν(C−H)]; 1649(s), 1613(m) [ν(C═N)]; 767(w), 724(w), 687(w) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 8.60 (s, 1H, NH_2), 8.00 (s, 1H, NH_2), 7.11 (s, br, 1H, N*H*), 3.09 (s, br, 6H, NMe_2), 2.73 (s, 3H, CH_3).



[**7b**](Cl)$_2$. Yield: 82%. Mp: 168 °C (dec). Anal. Calcd for $C_{20}H_{28}N_8Cl_2O_2Pt·{}^1/_2H_2O$: C, 34.94; H, 4.25; N, 16.30. Found: C, 35.08; H, 4.36; N, 16.26. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 303.593 ([M − 2Cl]$^{2+}$, calcd 303.596), 606.177 ([M − 2Cl − H]$^+$, calcd 606.185). IR (KBr, selected bonds, cm^{-1}): 3448(m), 3414(s), 3401(s), 3151(m) [ν(N−H)]; 2990(m), 2959(m), 2926(m) [ν(C−H)]; 1649(s) [ν(C═N)]; 1592(m) [ν(C═N) and/or ν(C═C_{Ar})]; 1570(w) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 778(w), 694(w) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 9.10 (s, 1H, NH_2), 8.84 (s, 1H, NH_2), 7.85−7.60 (m, 6H, N*H* + Ar), 2.73 (s, br, 6H, NMe_2). Crystals

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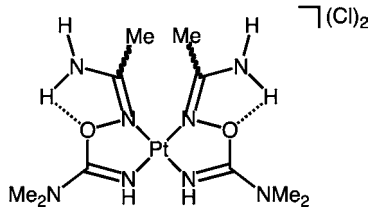
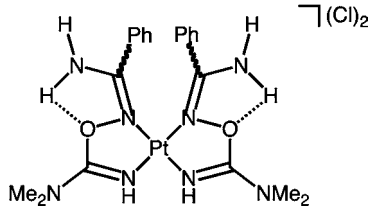
suitable for X-ray study were obtained by the slow evaporation of an ethanol solution of the complex at RT in air.

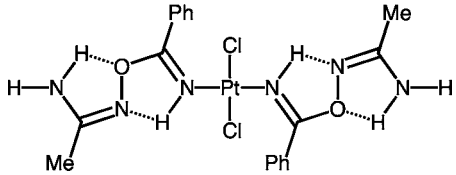


[**8a**]$(Cl)_2$. Yield: 62%. Mp: 156 °C (dec). Anal. Calcd for $C_{10}H_{24}N_8Cl_2O_2Pt{\cdot}2H_2O$: C, 20.34; H, 4.78; N, 18.98. Found: C, 20.46; H, 4.67; N, 18.87. High-resolution ESI^+-MS (MeOH, *m*/*z*): 482.149 ($[M - 2Cl - H]^+$, calcd 482.154). IR (KBr, selected bonds, cm^{-1}): 3406(s), 3246(m), 3150(m) [ν(N−H)]; 2935(w) ν(C−H); 1643(s) [ν(C═N)]; 726(w), 682(w) [δ(C−H)]. ^1H NMR (DMSO-d_6, δ): 8.70 (s, 1H, NH_2), 8.55 (s, 1H, NH_2), 8.01 (s, br, 1H, N*H*), 3.11 (s, br, 6H, NMe_2), 2.17 (s, 3H, CH_3).

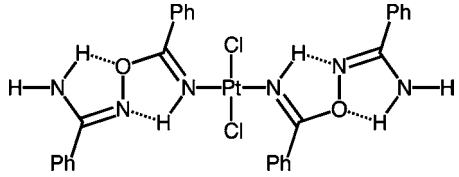


[**8b**]$(Cl)_2$. Yield: 75%. Mp: 142 °C (dec). Anal. Calcd for $C_{20}H_{28}N_8Cl_2O_2Pt{\cdot}2H_2O$: C, 33.62; H, 4.51; N, 15.68. Found: C, 33.43; H, 4.67; N, 15.68. High-resolution ESI^+-MS (MeOH, *m*/*z*): 303.597 ($[M - 2Cl]^{2+}$, calcd 303.596). IR (KBr, selected bonds, cm^{-1}): 3448(s) [ν(N−H)]; 2961(w), 2932(w), 2875(w) [ν(C−H)]; 1636(s) [ν(C═N) and/or ν(C═C_{Ar})]; 776(w), 690(w) [δ(C−H)]. ^1H NMR (DMSO-d_6, δ): 8.87 (s, br, 1H, N*H*), 8.25 (s, br, 1H, NH_2), 7.94 (s, br, 1H, NH_2), 7.67−7.60 (m, 3H, *o*- and *p*-C*H*), 7.49 (t, 2H, *m*-C*H*), 3.15 (s, 6H, NMe_2). Crystals suitable for X-ray study were obtained by the slow evaporation of a nitromethane solution of the complex at RT in air.

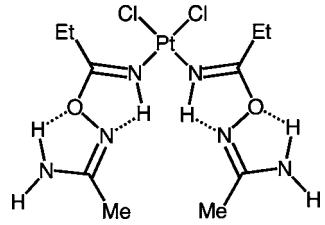
v. Nucleophilic Addition of 2 equiv of R′C(NH$_2$)═NOH (R′ = Me, Ph) to [PtCl$_2$(RCN)$_2$] (R = Et; Ph). A mixture of the amidoxime R′C(NH_2)═NOH (R′ = Me, Ph) (0.22 mmol) and *cis*- or *trans*-[$PtCl_2(RCN)_2$] (0.10 mmol; R = Et; Ph) was dissolved (**9d** and **10b**) or suspended (**9c**, **10a**, **10c**, and **10d**) in nitromethane (3 mL). The vigorously stirred suspension (or homogeneous solution without stirring for **9d** and **10b**) was kept for 24 h (R = Ph) or 48 h (for R = Et) at RT, whereupon the resulting suspension was cooled to 4 °C. The precipitate formed was filtered off, washed with two 1-mL portions of chloroform, and dried at RT in air.



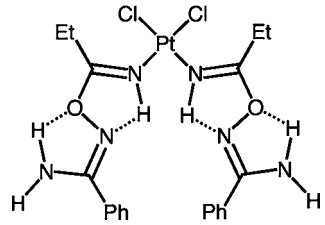
9c. Yield: 83%. Mp: 156 °C (dec). Anal. Calcd for $C_{18}H_{22}N_6Cl_2O_2Pt{\cdot}{}^1/_2H_2O$: C, 34.35; H, 3.68; N, 13.35. Found: C, 34.36; H, 3.66; N, 13.19. High-resolution ESI^+-MS (MeOH, *m*/*z*): 548.125 ($[M - 2Cl - H]^+$, calcd 548.132), 585.100 ($[M - Cl]^+$, calcd 585.109), 621.073 ($[M + H]^+$, calcd 621.085), 643.056 ($[M + Na]^+$, calcd 643.067), 1168.198 ($[2M - 2Cl - H]^+$, calcd 1168.210), 1205.173 ($[2M - Cl]^+$, calcd 1205.187), 1258.179 ($[2M + NH_4]^+$, calcd 1258.190), 1789.230 ($[3M - 2Cl - H]^+$, calcd 1789.288), 1861.219 ($[3M + H]^+$, calcd 1861.241), 1883.195 ($[3M + Na]^+$, calcd 1883.223). IR (KBr, selected bonds, cm^{-1}): 3494(m), 3354(m-s), 3188(m-s) [ν(N−H)]; 3056(w), 3003(w), 2968(w), 2925(w) [ν(C−H)]; 1669(m-s), 1623(vs) [ν(C═N)]; 1600(s) [ν(C═N) and/or ν(C═C_{Ar})]; 1576(s) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 778(m), 702(w), 690(m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 4:1, v/v): R_f = 0.35. ^1H NMR (DMSO-d_6, δ): 8.32 (d, 2H, *o*-C*H*), 8.18 (s, br, 1H, N*H*), 7.69 (t, 1H, *p*-CH), 7.57 (t, 2H, *m*-CH), 7.10 (s, br, 1H, N*H*), 6.84 (s, br, 1H, N*H*), 1.91 (s, 3H, CH_3).



9d. Yield: 87%. Mp: 143 °C (dec). Anal. Calcd for $C_{28}H_{26}N_6Cl_2O_2Pt{\cdot}H_2O$: C, 44.10; H, 3.70; N, 11.02. Found: C, 44.08; H, 3.52; N, 11.13. High-resolution ESI^+-MS (MeOH:Me_2SO = 10:1, *m*/*z*): 787.157 ($[M - Cl + Me_2SO]^+$, calcd 787.154). IR (KBr, selected bonds, cm^{-1}): 3491(m-s), 3340(m-s), 3283(m-s), 3258(sh) [ν(N−H)]; 3173 (w), 3055(w) [ν(C−H)]; 1622(vs) [ν(C═N)]; 1560(m-s) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 777(m-s), 696(s) [δ(C−H)]. TLC (eluent is chloroform:acetone = 10:1, v/v): R_f = 0.66. ^1H NMR (DMSO-d_6, δ): 8.90 (d, 2H, *o*-C*H*), 8.47 (s, br, 1H, N*H*), 7.85 (d, 2H, *o*-C*H*), 7.72 (t, 1H, *p*-CH), 7.63−7.50 (m, 5H, *m*- and *p*-CH), 7.39 (s, br, 2H, NH_2).



10a. Yield: 66%. Mp: 154 °C (dec). Anal. Calcd for $C_{10}H_{22}N_6Cl_2O_2Pt$: C, 22.91; H, 4.23; N, 16.03. Found: C, 22.78; H, 4.19; N, 16.14. High-resolution ESI^+-MS (MeOH, *m*/*z*): 452.133 ($[M - 2Cl - H]^+$, calcd 452.132), 489.111 ($[M - Cl]^+$, calcd 489.109), 525.093 ($[M + H]^+$, calcd 525.085), 542.147 ($[M + NH_4]^+$, calcd 542.112). IR (KBr, selected bonds, cm^{-1}): 3496(m), 3344(s), 3201(m) [ν(N−H)]; 3083(m), 2941(w-m), 2881(w) [ν(C−H)]; 1664(m-s), 1626(vs) [ν(C═N)]; 794(w), 700(w-m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 1:1, v/v): R_f = 0.62. ^1H NMR (DMSO-d_6, δ): 7.92 (s, br, 1H, N*H*), 6.90 (s, br, 1H, N*H*), 6.62 (s, br, 1H, N*H*), 2.89 (q, 2H, CH_2), 1.81 (s, 3H, CH_3), 1.25 (t, 3H, CH_3).



10b. Yield: 69%. Mp: 149 °C (dec). Anal. Calcd for $C_{20}H_{26}N_6Cl_2O_2Pt{\cdot}{}^3/_4H_2O$: C, 36.29; H, 4.19; N, 12.70. Found: C, 36.28; H, 4.17; N, 12.65. High-resolution ESI^+-MS (MeOH, *m*/*z*): 576.167 ($[M - 2Cl - H]^+$, calcd 576.163), 613.143 ($[M - Cl]^+$, calcd 613.140), 649.120 ($[M + H]^+$, calcd 649.117), 666.149 ($[M + NH_4]^+$, calcd 666.143), 687.077 ($[M + K]^+$, calcd 687.073), 1261.260 ($[2M - Cl]^+$, calcd 1261.249), 1314.263 ($[2M + NH_4]^+$, calcd 1314.253), 1335.203 ($[2M + K]^+$, calcd 1335.182). IR (KBr, selected bonds, cm^{-1}): 3496(m), 3373(m), 3299(s), 3227(m-s), 3185(m) [ν(N−H)]; 3059(w-m), 2988(w-m), 2941(w-m), 2918(w), 2888(w), 2849(w) [ν(C−H)]; 1671(s), 1629(vs) [ν(C═N)]; 1598(m) [ν(C═N) and/or ν(C═C_{Ar})]; 1567(s) [δ(N−H), ν(C═N), and/or ν(C═C_{Ar})]; 777(w), 695(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 4:1, v/v): R_f = 0.57. ^1H NMR (DMSO-d_6, δ): 8.38 (s, br, 1H, N*H*), 7.85

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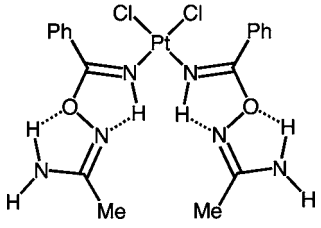
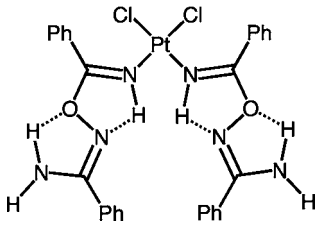
(d, 2H, *o*-C*H*), 7.55−7.40 (m, 3H, *m*- and *p*-CH), 7.16 (s, br, 2H, NH_2), 3.00 (q, 2H, CH_2), 1.35 (t, 3H, CH_3). Crystals suitable for X-ray study were obtained from the reaction mixture at RT in air.

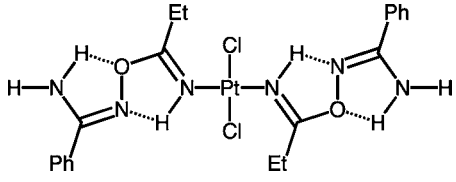


10c. Yield: 81%. Mp: 152 °C (dec). Anal. Calcd for $C_{18}H_{22}N_6Cl_2O_2Pt$: C, 34.85; H, 3.57; N, 13.55. Found: C, 34.91; H, 3.49; N, 13.47. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 621.090 ([M + H]$^+$, calcd 621.085), 643.073 ([M + Na]$^+$, calcd 643.067), 659.046 ([M + K]$^+$, calcd 659.041), 1241.175 ([2M + H]$^+$, calcd 1241.163), 1263.160 ([2M + Na]$^+$, calcd 1263.145), 1279.135 ([2M + K]$^+$, calcd 1279.119). IR (KBr, selected bonds, cm^{-1}): 3495(m-s), 3448(m), 3376(m-s), 3321(s), 3219(m-s), 3187(m-s) [ν(N−H)]; 3062(w), 2980(w), 2932(w) [ν(C−H)]; 1658(s), 1622(vs) [ν(C=N)]; 1598(m), [ν(C=N) and/or ν(C=C_{Ar})]; 1577(s) [δ(N−H), ν(C=N), and/or ν(C=C_{Ar})]; 785(m), 699(w) [δ(C−H)]. TLC (eluent is chloroform:acetone = 2:1, v/v): R_f = 0.44. ^{1}H NMR (DMSO-d_6, δ): 8.61 (d, 2H, *o*-C*H*), 7.79 (s, br, 1H, N*H*), 7.70−7.50 (m, 3H, *m*- and *p*-CH), 6.96 (s, br, 1H, N*H*), 6.64 (s, br, 1H, N*H*), 1.75 (s, 3H, CH_3).



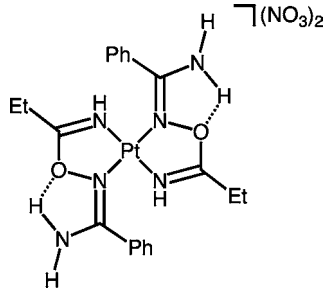
10d. Yield: 87%. Mp: 153 °C (dec). Anal. Calcd for $C_{28}H_{26}N_6Cl_2O_2Pt$: C, 45.17; H, 3.52; N, 11.29. Found: C, 45.01; H, 3.49; N, 11.42. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 709.147 ([M − Cl]$^+$, calcd 709.140), 745.123 ([M + H]$^+$, calcd 745.117), 767.107 ([M + Na]$^+$, calcd 767.096), 783.080 ([M + K]$^+$, calcd 783.073), 1453.262 ([2M − Cl]$^+$, calcd 1453.249), 1489.234 ([2M + H]$^+$, calcd 1489.226), 1511.221 ([2M + Na]$^+$, calcd 1511.208), 1527.197 ([2M + K]$^+$, calcd 1527.182). IR (KBr, selected bonds, cm^{-1}): 3482(m), 3363(m-s), 3288(m-s) [ν(N−H)]; 3059(w), 2922(w), 2859(w) [ν(C−H)]; 1636(s), 1612(vs) [ν(C=N)]; 1600(s) [ν(C=N) and/or ν(C=C_{Ar})]; 1578(s), 1570(s) [δ(N−H), ν(C=N), and/or ν(C=C_{Ar})]; 776(m), 694(m) [δ(C−H)]. TLC (eluent is chloroform:acetone = 8:1, v/v): R_f = 0.46. ^{1}H NMR (DMSO-d_6, δ): 8.72 (d, 2H, *o*-C*H*), 8.28 (s, br, 1H, N*H*), 7.73 (d, 2H, *o*-C*H*), 7.60−7.47 (m, 6H, *m*- and *p*-CH), 7.26 (s, br, 2H, NH_2).

vi. Preparation of [PtCl$_2$(HN=C(Et)ON=C(Ph)NH$_2$)$_2$]. A solution of the benzamidoxime PhC(NH_2)=NOH (0.2 mmol) in methanol (0.5 mL) was added to a solution of **5b** (0.10 mmol) in methanol (2 mL). The mixture was left to stand at RT. After 48 h, crystals formed were filtered off, washed with methanol (0.5 mL) and diethyl ether (1 mL), and dried at RT in air.

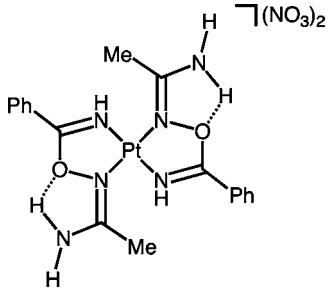


9b. Yield: 33%. Mp: 144 °C (dec). Anal. Calcd for $C_{20}H_{26}N_6Cl_2O_2Pt{\cdot}H_2O$: C, 36.04; H, 4.23; N, 12.61. Found: C, 35.88; H, 4.18; N, 12.57. High-resolution ESI$^+$-MS (MeOH:Me_2SO = 10:1, v/v, *m*/*z*): 671.111 ([M + Na]$^+$, calcd 671.098), 691.166 ([M − Cl + Me_2SO]$^+$, calcd 691.154), 1261.254 ([2M − Cl]$^+$, calcd 1261.249), 1319.213 ([2M + Na]$^+$, calcd 1319.208), 1339.267 ([2M − Cl + Me_2SO]$^+$, calcd 1339.263). IR (KBr, selected bonds, cm^{-1}): 3470(m), 3418(m), 3340(s), 3286(m-s) [ν(N−H)]; 3059(w-m), 2978(w-m), 2939(w-m), 2880(w), 2831(w) [ν(C−H)]; 1660(sh), 1626(vs) [ν(C=N)]; 1564(s) [δ(N−H), ν(C=N), and/or ν(C=C_{Ar})]; 781(m), 694(m) [δ(C−H)]. TLC (eluent is chloroform: acetone = 6:1, v/v): R_f = 0.57. ^{1}H NMR (DMSO-d_6, δ): 7.92 (s, br, 1H, N*H*), 7.81 (d, 2H, *o*-C*H*), 7.57−7.45 (m, 3H, *m*- and *p*-CH), 7.25 (s, br, 2H, NH_2), 3.02 (q, 2H, CH_2), 1.42 (t, 3H, CH_3). Crystals suitable for X-ray study were obtained from the reaction mixture at RT in air.

vii. Preparation of [Pt(HN=C(R)ON=C(R′)NH$_2$)$_2$](NO$_3$)$_2$ (R = Et, Ph; R′ = Me, Ph). A mixture of [PtCl$_2$(HN=C(R)ON=C(R′)NH$_2$)$_2$] (**9b**−**9d** and **10a**−**10d**; 0.05 mmol) and $AgNO_3$ (17 mg, 0.1 mmol) was suspended in MeOH (2 mL). The suspension was kept in the dark for 30 min under vigorous stirring, whereupon warm MeOH (10 mL, 55 °C) was added to the suspension to dissolve precipitated **7e** and then AgCl was filtered off. The filtrate was evaporated in vacuo, and the residue was washed with CH_2Cl_2 (1 mL) and Et_2O (1 mL).



[**7d**](NO_3)$_2$. Yield: ca. 100%. Mp: 175 °C (dec). Anal. Calcd for $C_{20}H_{26}N_8O_8Pt{\cdot}{}^1/_2H_2O$: C, 33.81; H, 3.83; N, 15.77. Found: C, 33.70; H, 3.44; N, 15.63. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 288.578 ([M − 2NO_3]$^{2+}$, calcd 288.585), 304.591 [M− 2NO_3 − H + MeOH]$^{2+}$, calcd 304.598), 576.152 ([M − 2NO_3 − H]$^+$, calcd 576.163), 608.178 ([M− 2NO_3 − H + MeOH]$^+$, 608.189). IR (KBr, selected bonds, cm^{-1}): 3432(s), 3427(s), 3367(s) [ν(N−H)]; 3055(m), 2927(w), 2853(w) [ν(C−H)]; 1669(m) [ν(C=N)]; 1636(s), 1588(s) [ν(C=N) and/or ν(C=C_{Ar})]; 1570(m) [δ(N−H), ν(C=N), and/or ν(C=C_{Ar})]; 1384(s) [ν(N−O)]; 780(w), 728(w), 706(w) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 9.23 (s, br, 1H, NH_2), 9.21 (s, br, 1H, NH_2), 7.84 (d, 2H, *o*-C*H*), 7.78 (t, 1H, *p*-C*H*), 7.68 (t, 2H, *m*-C*H*), 6.51 (s, br, 1H, N*H*), 2.46 (q, 2H, CH_2), 0.84 (t, 3H, CH_3). Crystals suitable for X-ray study were obtained by the slow evaporation of an ethanol−nitromethane (1:1, v/v) solution at RT in air.



[**7e**](NO_3)$_2$. Yield: ca. 100%. Mp: 173 °C (dec). Anal. Calcd for $C_{18}H_{22}N_8O_8Pt$: C, 32.10; H, 3.29; N, 16.64. Found: C, 32.23; H, 3.39; N, 16.52. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 274.574 ([M − 2NO_3]$^{2+}$, calcd 274.570), 548.134 ([M − 2NO_3 − H]$^+$, calcd 548.132). IR (KBr, selected bonds, cm^{-1}): 3385(m), 3342(m), 3313(m), 3171(m-s) [ν(N−H)]; 2947(w) [ν(C−H)]; 1668(m), 1632(s) [ν(C=N)]; 1601(s) [ν(C=N) and/or ν(C=C)]; 1580(m-s) [δ(N−H), ν(C=N), and/or ν(C=C_{Ar})]; 1384(vs) [ν(N−O)];

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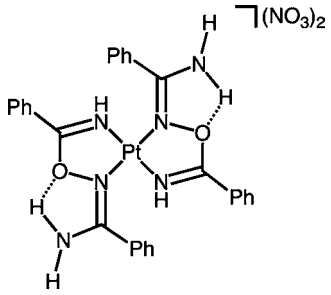
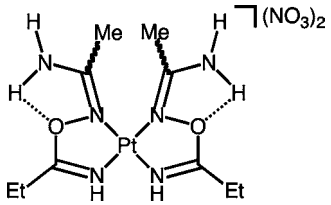
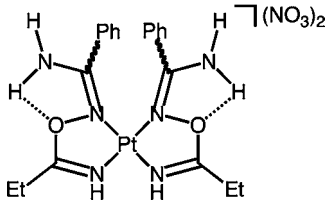
777(w-m), 689(m) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 10.73 (s, br, 1H, N*H*), 8.95 (s, br, 1H, NH_2), 8.71 (s, br, 1H, NH_2), 8.20 (d, 2H, *o*-C*H*), 7.83 (m, 1H, *p*-C*H*), 7.66 (t, 2H, *m*-C*H*), 1.24 (s, 3H, CH_3).



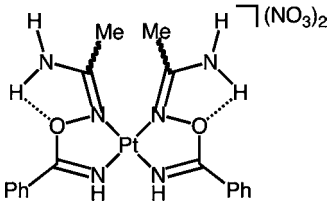
[**7f**](NO$_3$)$_2$. Yield: ca. 100%. Mp: 177 °C (dec). Anal. Calcd for $C_{28}H_{26}N_8O_8Pt\cdot{}^1/_2H_2O$: C, 41.69; H, 3.37; N, 13.89. Found: C, 41.51; H, 3.41; N, 13.82. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 336.587 ([M − 2NO$_3$]$^{2+}$, calcd 336.585), 672.167 ([M − 2NO$_3$ − H]$^+$, calcd 672.163). IR (KBr, selected bonds, cm^{-1}): 3421(m-s), 3366(s), 3186(m-s) [ν(N−H)]; 3053(w), 2960(w), 2925(w), 2854(w) [ν(C−H)]; 1622(vs) [ν(C═N)]; 1601(vs) [ν(C═N) and/or ν(C═C$_{Ar}$)]; 1560(m) [δ(N−H), ν(C═N), and/or ν(C═C$_{Ar}$)]; 1384(s) [ν(N−O)]; 787(m), 692(m) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 9.37 (s, br, 1H, NH_2), 9.35 (s, br, 1H, NH_2), 7.99−7.97 (d + s, br, 3H, *o*-C*H* + N*H*), 7.86−7.77 (m, 2H, 2*p*-C*H*), 7.72 (t, 2H, *m*-C*H*), 7.63−7.58 (m, 4H, *o*- and *m*-C*H*).



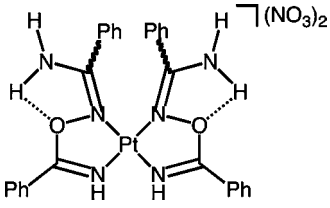
[**8c**](NO$_3$)$_2$. Yield: ca. 100%. Melting point and microanalytical data were not obtained because of the relatively fast decomposition of **35** right after the preparation. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 226.567 ([M − 2NO$_3$]$^{2+}$, calcd 226.572), 452.129 ([M − 2NO$_3$ − H]$^+$, calcd 452.137). IR (KBr, selected bonds, cm^{-1}): 3434(m-s), 3337(m), 3170(m) [ν(N−H)]; 2985(w), 2920(w), 2853(w) [ν(C−H)]; 1638(vs), 1592(m) [ν(C═N)]; 1565(m-s) [δ(N−H) and/or ν(C═N)]; 1384(vs) [ν(N−O)]; 793(w), 666(w) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 10.48 (s, br, 1H, N*H*), 8.88 (s, br, 1H, NH_2), 8.65 (s, br, 1H, NH_2), 2.81 (q, 2H, CH_2), 2.24 (s, 3H, CH_3), 1.23 (t, 3H, CH_3).



[**8d**](NO$_3$)$_2$. Yield: ca. 100%. Melting point and microanalytical data were not obtained because of the relatively fast decomposition of **35** right after the preparation. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 288.578 ([M − 2NO$_3$]$^{2+}$, calcd 288.585), 576.151 ([M − 2NO$_3$ − H]$^+$, calcd 576.163). IR (KBr, selected bonds, cm^{-1}): 3433(m-s), 3329(m), 3159(m) [ν(N−H)]; 3059(w-m), 2990(w), 2946(w) [ν(C−H)]; 1653(s), 1630(vs) [ν(C═N)]; 1596(s) [ν(C═N) and/or ν(C═C$_{Ar}$)]; 1565(m-s) [δ(N−H), ν(C═N), and/or ν(C═C)]; 1384(vs) [ν(N−O)]; 774(m), 698 (m) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 10.50 (s, br, 1H, N*H*), 8.45 (s, br, 1H, NH_2), 8.43 (s, br, 1H, NH_2), 7.67 (d, 2H, *o*-C*H*), 7.58−7.47 (m, 3H, *m*- and *p*-C*H*), 2.84 (q, 2H, CH_2), 1.29 (t, 3H, CH_3).



[**8e**](NO$_3$)$_2$. Yield: ca. 100%. Mp: 139 °C (dec). Anal. Calcd for $C_{18}H_{22}N_8O_8Pt\cdot2H_2O$: C, 34.38; H, 4.85; N, 14.58. Found: C, 34.37; H, 4.95; N, 14.50. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 274.569 ([M − 2NO$_3$]$^{2+}$, calcd 274.570), 548.142 ([M − 2NO$_3$ − H]$^+$, calcd 548.132). IR (KBr, selected bonds, cm^{-1}): 3443(m-s), 3328(m-s), 3149(m) [ν(N−H)]; 2922(w), 2849(w) [ν(C−H)]; 1654(m), 1623(s) [ν(C═N)]; 1576(m-s) [δ(N−H), ν(C═N), and/or ν(C═C$_{Ar}$)]; 1384(vs) [ν(N−O)]; 780(w-m), 687(m) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 11.05 (s, br, 1H, N*H*), 9.04 (s, br, 1H, NH_2), 8.72 (s, br, 1H, NH_2), 8.22 (d, 2H, *o*-C*H*), 7.86 (t, 1H, *p*-C*H*), 7.70 (t, 2H, *m*-C*H*), 2.37 (s, 3H, CH_3).



[**8f**](NO$_3$)$_2$. Yield: ca. 100%. Mp: 156 °C (dec). Anal. Calcd for $C_{28}H_{26}N_8O_8Pt\cdot3{}^1/_4H_2O$: C, 39.28; H, 3.83; N, 13.09. Found: C, 39.10; H, 3.54; N, 13.22. High-resolution ESI$^+$-MS (MeOH, *m*/*z*): 336.578 ([M − 2NO$_3$]$^{2+}$, calcd 336.585), 672.158 ([M − 2NO$_3$ − H]$^+$, calcd 672.163). IR (KBr, selected bonds, cm^{-1}): 3429(m-s), 3316(m-s), 3134(m) [ν(N−H)]; 2935(w), 2854(w) [ν(C−H)]; 1654(m), 1626(s) [ν(C═N)]; 1596(s) [ν(C═N) and/or ν(C═C$_{Ar}$)]; 1558(s) [δ(N−H), ν(C═N), and/or ν(C═C)]; 1384(vs) [ν(N−O)]; 774(w-m), 693(m) [δ(C−H)]. ^{1}H NMR (DMSO-d_6, δ): 11.23 (s, br, 1H, N*H*), 8.64 (s, br, 1H, NH_2), 8.62 (s, br, 1H, NH_2), 8.26 (d, 2H, *o*-C*H*), 7.87 (t, 1H, *p*-C*H*), 7.78−7.68 (m, 5H, C*H*), 7.57 (t, 2H, *m*-C*H*). Crystals suitable for X-ray study were obtained by the slow evaporation of an ethanol−nitromethane (1:1, v/v) solution at RT in air.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, molecular structures, and tables of crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Due to a production error, this paper was published on the Web on May 8, 2012, with minor text errors. The corrected version was reposted on May 10, 2012.